

Theoretical study of structural, electronic, magnetic and mechanical
properties of Ru-based alloys

By

Mnisi Bhila Oliver

Submitted in accordance with the requirement for
the degree of

DOCTOR OF PHILOSOPHY

In the subject

Physics

at the

UNIVERSITY OF SOUTH AFRICA

SUPERVISOR: Dr M.M. TIBANE

CO-SUPERVISOR: Prof E.M. BENECHA

September 2026

Declaration
(Student number: 55792235)

“I hereby declare that the theoretical study of the structural, electronic, magnetic, and mechanical properties of Ru-based alloys is my original work. All sources used or quoted have been properly indicated and acknowledged with complete references”.



Signature

September 2026

Date

Dedication

This PhD thesis is dedicated to all those who are less fortunate.

Acknowledgement

I sincerely thank God for granting me strength, wisdom, health, and patience throughout this journey. I sincerely appreciate my supervisors, Dr. M.M. Tibane and Prof. E.M. Benecha, whose invaluable guidance and support made this thesis possible.

I also extend my gratitude to the National Research Foundation and the UNISA Masters and Doctoral Bursaries for their financial support.

I would also like to thank my family and my partner for their unwavering support throughout this journey. Additionally, I extend my gratitude to the members of the physics department for their contributions and encouragement.

Abstract

Superalloys are high-performance materials known for their exceptional tolerance to oxidizing environments and ability to withstand high-temperatures. Composed mainly of nickel, iron, or cobalt, these alloys play a critical role in a wide range of high-temperature performance applications. Notably, nickel-based superalloys (NBSAs) are widely used in the hot-section components of gas turbine engines due to their outstanding structural and mechanical properties at elevated temperatures. These properties include high mechanical strength, a high melting point, relatively low density, excellent thermal and surface stability, and resistance to corrosion and oxidation. Despite their success, NBSAs have already reached 90% of nickel's melting point, limiting their application in next-generation gas turbine engines. Therefore, there is an urgent need to investigate alternative materials with melting points exceeding that of nickel. The development of such materials could significantly enhance engine efficiency while reducing energy consumption and greenhouse gas emissions.

Density Functional Theory (DFT) was employed to investigate the structural, magnetic, mechanical, and electronic properties of $X_3\text{Ru}$ alloys ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) in the A15, D0c, and tP16 crystal phases. Among the systems investigated, the A15 Cr_3Ru alloy emerges as the most thermodynamically favorable compound under equilibrium conditions. In addition, it exhibits a combination of outstanding properties, including relatively low density, excellent mechanical stability, good ductility, a high bulk modulus, and a superior melting temperature exceeding that of the commonly used $\text{L1}_2\text{-Ni}_3\text{Al}$ alloy. These attributes position A15 Cr_3Ru as a strong candidate for high-temperature applications, where resistance to plastic deformation and the ability to maintain structural integrity under applied loads are critical. Its remarkable compression resistance coupled with relatively low density further supports its suitability for lightweight, high-strength applications.

Although alloys such as A15 Ti_3Ru , A15 V_3Ru , A15 Co_3Ru , D0c Co_3Ru , D0c Fe_3Ru , and tP16 Fe_3Ru are predicted to be thermodynamically unstable, as indicated by their positive heats of formation, the results highlight that these systems nevertheless exhibit desirable attributes. Their high melting temperatures, ductility, magnetic behavior, elevated bulk moduli, and low densities

underscore their potential to meet the performance requirements of advanced engineering applications. The observed resistance to compression and structural collapse positions these alloys as promising candidates for high-temperature environments, while their magnetic properties broaden their applicability to electronics, telecommunications, energy production, and medical imaging. These findings demonstrate that, despite inherent instability, the alloys possess key functional characteristics that directly address the objectives of this study and reinforce their relevance in the search for materials with multifunctional capabilities.

Density of states analysis further confirms the metallic nature of all studied systems, ensuring efficient electron transport and reinforcing their suitability for electronic and energy-related applications. Importantly, while only $\text{Al}_{15}\text{Cr}_3\text{Ru}$ has been experimentally synthesized to date, the theoretical predictions presented here provide a roadmap for future experimental efforts. Successful synthesis of these alloys could enable their application as protective coatings or as substitutes for nickel-based superalloys in next-generation turbine engines, thereby enhancing efficiency, reducing energy consumption, and mitigating greenhouse gas emissions.

Overall, the novelty of this work lies in identifying Ru-based alloys that combine high-temperature resilience, mechanical strength, and multifunctional properties, while simultaneously expanding the design space beyond conventional nickel-based systems. These insights contribute meaningfully to the advancement of high-performance materials and open new avenues for engineering applications across aerospace, energy, electronics, and medical technologies.

List of Publications

The following papers have been included in the thesis

1. Mnisi, B.O., Benecha, E.M., Chauke, H.R., Ngoepe, P.E. and Tibane, M.M., 2020. Effect of transition metal doping on Cr–Ru alloys using first principles approach. *Bulletin of Materials Science*, 43, pp.1-9.
2. Mnisi, B.O., Benecha, E. M. and Tibane, M. M. 2024. Investigation of the thermodynamic, structural, electronic, mechanical and phonon properties of D0c Ru-based intermetallic alloys: An ab-initio Study. *Materials Research Express*, 11(4), pp. 1-13.
3. Mnisi, B.O., Benecha, M.E. and Tibane, M.M., 2024. First-Principles Study on Thermodynamic, Structural, Mechanical, Electronic and Phonon Properties of tP16 Ru-Based Alloys. *Alloys*, 3(2), pp.126-139.
4. Mnisi, B.O., Benecha, M.E. and Tibane, M.M., Effect of pressure on structural, electronic, and mechanical properties of tP16 Cr₃Ru intermetallic alloy: A first principles density functional theory study in the Proceedings of SAIP2024, the 68th Annual Conference of the South African Institute of Physics, edited by Prof. Aletta Prinsloo, (UJ), pp. 129-134. ISBN: 978-1-0370-2645-4. Available online at <http://events.saip.org.za>.
5. Mnisi, B.O., Benecha, M.E. and Tibane, M.M., Density functional theory study on the effect of pressure on structural, mechanical and phonon properties of A15 Mn₃Ru compound, in The Proceedings of SAIP2025, the 69th Annual Conference of the South African Institute of Physics, edited by W. A. Horowitz, (UCT), pp. 202-208. ISBN: 978-1-0492-1-0492-1907-3. Available online at <http://events2.saip.org.za>.
6. Mnisi, B.O., Benecha, E.M. and Tibane, M.M., 2025. Stability of Novel D0c Mn₃Ru Alloy Under Variable Pressure Conditions: A First-Principles DFT Study. *JOM*, 77 (11) pp. 8360-8367.

Papers not included in the thesis

7. Mnisi, B.O., Benecha, E.M. and Tibane, M.M., 2025. Density functional theory study of phase stability and electronic properties for L1₂ X₃Ru and XRu₃ alloys. *The European Physical Journal B*, 98(5), pp.1-16.
8. Mnisi, B.O., Benecha, E.M. and Tibane, M.M., 2024. First-principles study of stability and electronic properties of B2 X–Ru alloys for high-temperature structural applications. *Materials Advances*, 5(13), pp.5632-5643.
9. Ali, I.O.A., Mnisi, B.O, Benecha, M.E. and Tibane, M.M., First-principles study of the Structural, Mechanical, Dynamical, Electronic and Lattice Thermal Conductivity properties of HfSnPt: A half-Heusler alloy, in the Proceedings of SAIP2025, the 69th Annual Conference of the South African Institute of Physics, edited by W. A. Horowitz, (UCT), pp. 210-216. ISBN: 978-1-0492-1-0492-1907-3. Available online at <http://events2.saip.org.za>.
10. Mnisi, B.O., Benecha, E.M. and Tibane, M.M., 2021. Density functional theory studies of structural, electronic, and optical properties of cubic 3d-transition metal nitrides. *Intermetallics*, 137, pp.1-13.
11. Mnisi, B.O., 2022. Density functional theory study of electronic and optical properties of ScN nitride in NaCl-B1, CsCl-B2, ZB-B3 and NiAs-B8 phases. *Bulletin of Materials Science*, 45(1), pp.1-9.

12. Mnisi, B.O., 2024. Ab initio study of phase stability and optical properties of TiN and VN nitrides in different phases. *Solid State Communications*, 377, pp.1-11.
13. Mnisi, B. O. 2021. Density functional theory study of structural, mechanical, electronic and optical properties of MoAlX (X= B, C, N and O) compounds. *Materials Research Express*, 8(9), pp. 1-13.
14. Mnisi, B. O., and Tibane, M. M. 2024. ZrN doped with 3d transition metals: a computational investigation of main physical properties for high-temperature structural applications. *Materials Research Express*, 11(5), pp. 1-14.
15. Mnisi, B.O., 2025. DFT study on phase stability of CrB, MoB, and WB in α , β phases, and CrB₂, MoB₂, and WB₂ in hP6 phase. *Vacuum*, 234, pp.1-13.
16. Mnisi, B.O. 2025. Density functional theory study on structural, mechanical, electronic, and phonon properties of CrAlB, MoAlB, WAlB, CrAlGa, MoAlGa, and WAlGa ternary compounds. *The European Physical Journal B*, 98(3), pp. 1-19.
17. Ali, I.O.A., Mnisi, B.O., Benecha, E.M. and Tibane, M.M., 2025. Phase stability and physical properties of XSnPt (X= Ti, Zr, Hf): A density functional theory study. *Physics Open*, 25, pp.1-11.
18. Mnisi, B.O., Ali, I.O.A., Benecha, E.M. and Tibane, M.M., 2026. First-principles density functional theory study of physical properties of half-Heusler XSnPt compounds (X= V, Nb, and Ta) for high-temperature structural application. *Bulletin of Materials Science*, 49(3), pp1-15.
19. Ali, I.O.A., Mnisi, B.O., Benecha, E.M. and Tibane, M.M., 2026. Comprehensive Investigation of Structural, Mechanical, Electronic, Phonon, Thermal, and Optical Properties of CrSnX (X= Pd, Pt) Half-Heusler Alloys: An Ab Initio Study. *Journal of Electronic Materials*, 55, pp.1-18.
20. Mnisi, B.O., Ali, I.O.A, Benecha, E.M. and Tibane, M.M., 2026 Phase stability and electronic property of PtY, Pt₂Y, Pt₃Y, PtSc and Pt₃Sc in cubic phase and PtY, PtY₂, PtY₃ and PtSc₂ in orthorhombic phase: A first-principles DFT study. *Materials today communications*, 51, pp 1-15.
21. Mnisi, B.O., Benecha, E.M. and Tibane, M.M. Density Functional Theory study of the phase stability in tP16 Cr₃Ru and Mn₃Ru Alloys under pressure for High-Temperature Applications. *Materials* (MDPI), (Under review).
22. Ali, I.O.A., Mnisi, B.O, Benecha, E.M. and Tibane, M.M., 2026 the Density Functional Theory Study on the structural, mechanical, phonon, electronic and thermodynamical Properties of Ti₆X₂B (X = Si, Sn, Pb, N, P, As, Sb) for Advanced Functional Applications. *Computation condensed matter*, 48, pp-1-18).
23. Mnisi, B.O, Ali, I.O.A, Modiba R, Benecha, E.M. and Tibane M.M. First principles density functional study on phase stability, electronic and thermal properties of the Sc₆X₂B (X = N, P, As, Sb, Si, Sn, Pb) compounds. *Material Advances*. (Under review).
24. Ali, I.O.A, Mnisi, B.O, Modiba R, Benecha, E.M. and Tibane M.M. F First principles density functional study on stability, electronic and thermodynamical properties of V₁₀Si₆B, V₅Si₃B and V₅Si₂B, compounds for high temperature structural applications *Materials today communication*. (Under review).

Book chapter included in the thesis

25. Mnisi, B.O., Benecha, E.M. and Tibane, M.M., 2021. Computational study of A15 Ru-based alloys for high-temperature structural applications. In *Ruthenium-An Element Loved by Researchers*. Intechopen, pp. 1-20.

Contents

Acknowledgement.....	iv
Abstract	v
List of Publications.....	vii
List of Tables.....	xii
List of Figures.....	xv
Chapter One.....	26
Introduction.....	26
1.1 General introduction.....	26
1.2 Problem statement	27
1.3 Aims and Objectives	29
1.4 Thesis Outline.....	29
Chapter Two	31
Literature review	31
2.1 Overview	31
2.2 Gas turbine engine	31
2.3 High-temperature structural materials	34
2.3.1 Pt-based alloys.....	35
2.3.2 Niobium-based alloys	36
2.3.3 Refractory high entropy alloys	37
2.3.4 Ti- based alloys	37
2.3.5 Cr based alloys	38
2.3.6 Ru-based alloys.....	41
2.3.7 Pt-Ga, Pt-Al, Pt-Cr and Ru-Cr in L1 ₂ , D0 _c , D0' _c and tP16 phases	42
2.4 Physical and structural properties of 3d transition metal elements	47
2.5 Structural properties of A15, D0_c and tP16 crystallographic phases.....	48
2.5.1 A15 phase.....	48
2.5.2 D0 _c phase	49
2.5.3 tP16 phase	50
2.6 Conclusion.....	50

Chapter Three	52
Computational methodology	52
3.1 The many-body problem	52
3.2 Density Functional Theory	54
3.3 The Exchange-Correlation Functional	56
3.3.1 Local Density Approximation	57
3.3.2 Generalized Gradient Approximation	59
3.3.3 Generalized Gradient Approximation with the Hubbard Parameter (GGA + U)	60
3.4 The Hartree Potential	61
3.4.1 Full potential approach	61
3.4.2 Pseudopotential approach	62
3.5 Non-linear core correction in pseudopotential approximations	67
3.6 Numerical implementation of the Kohn-Sham equations	68
3.7 Other important aspects in solving the Kohn-Sham equations	69
3.8 Geometry optimization	71
3.9 Brillouin zone sampling	74
3.10 Computational code	75
3.10.1 Material studio	75
3.11. Accuracy and reliability of DFT calculations	76
Chapter Four	78
Structural, electronic and mechanical stability of X₃Ru in A15, D0c and tP16 in crystallographic phases	78
4.1 Computational parameters	79
4.2 Thermodynamic stability	83
4.3 Density	91
4.4 Electronic and magnetic properties	93
4.4.1 Spin polarization and magnetization	95
4.4.2 Metallic characteristics and conductivity	103

4.4.3 Hybridization and bonding characteristics	104
4.5 Mechanical properties	104
4.5.1 Elastic constants	105
4.5.2 Bulk, Shear and Young's moduli	109
Chapter Five.....	130
Pressure dependent structural stability, electronic and mechanical stability of X_3Ru ($X = Cr, Mn$) in A15, D0c and tP16 crystallographic phases	130
5.1 Brief literature on related alloys under pressure.....	131
5.2 Structural stability of Cr_3Ru and Mn_3Ru under pressure.....	131
5.2.1 Induced magnetic moments	138
5.2.2 Density.....	140
5.3 Electronic and magnetic properties.....	141
5.3.1 Spin polarization and magnetization.....	142
5.3.2 Metallic characteristics and conductivity	142
5.3.3 Hybridization and bonding characteristics.....	144
5.4 Mechanical properties	152
5.4.1 Bulk, Shear and Young's moduli	156
5.4.2 Ductility	164
5.4.3 Poisson's ratio	165
5.4.4 Elastic anisotropy	166
5.4.5 Melting point temperature	167
Chapter Six	170
6.1 Summary and Conclusion	170
6.2 Limitations and recommendations of the study	173
Appendix.....	174
References	178

List of Tables

Table 2.1: Properties, applications and limitations of the metallic based alloys such as nickel, platinum, niobium, titanium and refractory high-entropy alloys.....	41
Table 1.2: Physical properties of Ni, Cu, V, Fe, Cr, Mn, Sc, Ti, Co, Zn and Ru transition metals.....	48
Table 2.3: The atomic positions in the A15, D0c and tP16 X_3Ru ($X = Sc-Zn$). The displacement parameter U in this case.....	51
Table 4.1: Calculated lattice parameters and magnetic moments of studied pure 3d-transition metal (X) and ruthenium compared to experimental data where available.....	81
Table 4.2: Optimized equilibrium lattice parameter, heat of formation, magnetic moments, density and bond-length X-Ru (in Å) of A15-type X_3Ru	85
Table 4.3: Optimized equilibrium lattice parameters, heat of formation, magnetic moments, density and bond-length X-Ru (in Å) of D0c-type X_3Ru alloys.....	86
Table 4.4: Optimized equilibrium lattice parameter, heat of formation, magnetic moments, density and bond-length X-Ru in Å of tP16-type X_3Ru alloys	86
Table 4.5: The atomic radii, atomic radii difference, magnetic moments, electronic configuration and number of paired electrons of 3d transition metal from Sc-Zn bonded with central Ru atom.....	87
Table 4.6: Computed elastic constants (C_{ij}), average elastic moduli of bulk modulus B, shear modulus G and Young's modulus E in Voigt, Reuss and Hill approximation for A15 X_3Ru compounds. All elastic constants and modulus are in GPa	180
Table 4.7: Computed elastic constants (C_{ij}), Shear moduli (C'), average elastic moduli of bulk modulus B, shear modulus G and Young's modulus E in Voigt, Reuss and Hill approximation for D0c X_3Ru compounds. All elastic constants and moduli are reported in GPa.....	110
Table 4.8: Computed elastic constants (C_{ij}), average elastic moduli of bulk modulus B, shear modulus G and Young's modulus E in Voigt, Reuss and Hill approximation for tP16 X_3Ru compounds. All elastic constants and moduli are reported in GPa	112
Table 4.9: The calculated B/G ratio, melting temperature (T_m) in kelvin, crystal anisotropy (A^U) and hardness (H_V) for A15 phase.	118

Table 4.10: The calculated B/G ratio, melting temperature (T_m) in kelvin, crystal anisotropy (A^U) and hardness (H_v) for D0c phase.	118
Table 4.11: The calculated B/G ratio, Shear moduli (C'), melting temperature (T_m) in kelvin, crystal anisotropy (A^U) and hardness (H_v) for tP16 phase.....	119
Table 4.12: Melting temperatures (K) for elemental 3d-transition metals and commonly used alloys for high-temperature structural applications provided for reference.	125
Table 4.13: The calculated melting temperature T_m under low- and high-pressure conditions for Cr_3Ru in A15, D0c and tP16 phases.....	125
Table 5.2: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of A15, Mn_3Ru at different pressures.....	134
Table 5.2: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of A15, Cr_3Ru at different pressures.....	135
Table 5.3: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of D0c, Mn_3Ru structure at different pressures.....	135
Table 5.4: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of D0c, Cr_3Ru at different pressures.....	136
Table 5.5: The calculated lattice constants, heat of formation, magnetic moment, density and bond-length of tP16, Mn_3Ru at different pressures.....	137
Table 5.6: The calculated lattice constants, heat of formation, magnetic moment, density and bond-length of tP16, Cr_3Ru at different pressures.....	137
Table 5.7: The calculated elastic constants for A15 Mn_3Ru . All the elastic constants are in GPa under zero and varying pressure conditions.....	153
Table 5.8: The calculated elastic constants for A15 Cr_3Ru . All the elastic constants are in GPa under zero and varying pressure conditions.....	153
Table 5.9: The calculated elastic constants for D0c Mn_3Ru . All the elastic constants are in GPa under zero and varying pressure.....	154
Table 5.10: The calculated elastic constants for D0c Cr_3Ru . All the elastic constants are in GPa under zero and varying pressure conditions.....	154
Table 5.11: The calculated elastic constants for tP16 Mn_3Ru . All the elastic constants are in GPa under zero and varying pressure conditions. All the elastic constants are in GPa	155
Table 5.12: The calculated elastic constants for tP16 Cr_3Ru under zero and varying pressure conditions. All the elastic constants are in GPa.....	155

Table 5.13: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Voigt, Reuss and Hill approximations, Poisson ratio, for A15 Mn ₃ Ru. All the elastic moduli are in GPa, The melting temperature (K) and universal elastic anisotropy under zero and varying pressure conditions.....	158
Table 5.14: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Hill approximation, Poisson ratio, Cauchy pressure (C ₁₂ -C ₄₄), melting temperature (K) and universal elastic anisotropy for A15 Cr ₃ RuThe under zero and varying pressure conditions.....	159
Table 5.15: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Hill approximation and Poisson ratio all the elastic moduli are in GPa. We also calculate the melting temperature (K) and universal elastic anisotropy for D0c Mn ₃ Ru under zero and varying pressure conditions.....	159
Table 5.16: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Hill approximation and Poisson ratio all the elastic moduli are in GPa. We also calculate the melting temperature (K) and universal elastic anisotropy for D0c Cr ₃ Ru under zero and varying pressure conditions.....	160
Table 5.17: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Voigt, Reuss and Hill approximations, Poisson ratio for tP16 X ₃ Ru (X = Cr and Mn). All the elastic moduli are in GPa, The melting temperature (K) and universal elastic anisotropy.....	162
Table 5.18: The calculated melting temperature T _m under low- and high-pressure conditions for Mn ₃ Ru in A15, D0c and tP16 phases.....	168
Table 5.19 Summary of the computational parameters used in this study for A15, D0c and tP16 X ₃ Ru (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) alloys	168

List of Figures

Figure 2.1: Illustration of the main components of the commercial aircraft turbine engine.....	33
Figure 2.2: Illustration of turbine blade showing holes for cooling.....	33
Figure 2.3: Illustration of Cr-Ru phase diagram.....	44
Figure 2.4: Ball-and-stick illustration of the different crystal structure phases of X–Ru alloys. Pink spheres represent atoms of X (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn), while blue spheres represent Ru atoms	49
Figure 3.1: Kohn-Sham-DFT equation and its implementation.....	56
Figure 3.2: Schematic delineation of the pseudo-potential model. The dense lines display the all-electron wave-function, $\psi^{AE}(r)$, and ionic potential, $v_{ion}^{AE}(r)$, while the dashed lines show the relating pseudo-wave-function, $\psi^{PS}(r)$, given by the pseudo potential, $v_{ion}^{PS}(r)$. All quantities appeared as a function of distance, r , from the atomic nucleus.....	63
Figure 3.3: Schematic representation of the SCF method used in DFT.....	69
Figure 4.1: Crystal structure of (a) cubic A15, (b) D0c and (c) tP16 phase of Ru-Cr alloys: Green balls represent-Ru atoms while gray balls represent Cr atoms.	80
Figure 4.2: The total energy difference versus the energy cutoff for A15, D0c and tP16 Cr ₃ Ru alloys...82	82
Figure 4.3: Total energy difference versus the K-points for A15, D0c and tP16 Cr ₃ Ru alloys.....	82
Figure 4.4: Calculated (a) lattice parameters (Å), (b) heat of formation (eV/atom), (c) magnetic moments (μ_B /atom), (d) density (g/cm ³) and (e) bond-length (Å) for A15, D0c and tP16 X ₃ Ru (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) compounds.	90
Figure 4.5 (a): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary A15 3d-X ₃ Ru transition metal (X = Sc, Ti, V, Cr and Mn) calculated from GGA functional. Fermi energy is set to zero in each compound.....	97
Figure 4.5 (b): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary A15 3d-X ₃ Ru transition metal (X = Fe, Co, Ni, Cu and Zn) calculated from GGA functional. Fermi energy is set to zero in each compound.....	98
Figure 4.6 (a): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary D0c 3d-X ₃ Ru transition metal (X = Sc, Ti, V, Cr and Mn) calculated from GGA functional. Fermi energy is set to zero in each compound.....	99
Figure 4.6 (b): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary D0c 3d-X ₃ Ru transition metal (X = Fe, Co, Ni, Cu and Zn) calculated from GGA functional. Fermi energy is set to zero in each compound.....	100

Figure 4.7 (a): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary tP16 3d- X_3 Ru transition metal ($X = \text{Sc, Ti, V, Cr and Mn}$) calculated from GGA functional. Fermi energy is set to zero in each compound.....	101
Figure 4.7 (b): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary tP16 3d- X_3 Ru transition metal ($X = \text{Fe, Co, Ni, Cu and Zn}$) calculated from GGA functional. Fermi energy is set to zero in each compound. All the alloys have the same vertical scale except Zn_3Ru	102
Figure 4.8: Calculated melting temperatures (T_m) of (a) A15, (b) D0c and (c) tP16 $X_3\text{Ru}$ structures. The brown dotted line represents Ni_3Al (1691 K) whilst the green dotted line represents Nb_3Al (2333 K).	126
Figure 4.9: Calculated trends in melting temperatures (T_m) of (a) A15, (b) D0c and (c) tP16 $X_3\text{Ru}$ structures. The red dotted line represents Ni_3Al (1691 K) whilst the green dotted line represents Nb_3Al (2333 K)	128
Figure 4.10: The calculated melting temperature T_m under low- and high-pressure conditions for Cr_3Ru in A15, D0c and tP16 phases.....	102
Figure 4.11: The spin-polarized partial density of states (PDOS) of Ru in all A15-type 3d- $X_3\text{Ru}$ transition compounds ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) was calculated using the GGA functional. The Fermi energy for each compound is set to zero. Additionally, the y-axis of the Ru PDOS has been magnified to better visualize the contributions from the deep s, p, and d states.....	105
Figure 4.12: The spin-polarized partial density of states (PDOS) of Ru in all D0c-type 3d- $X_3\text{Ru}$ transition compounds ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) was calculated using the GGA functional. The Fermi energy for each compound is set to zero. Additionally, the y-axis of the Ru PDOS has been magnified to better visualize the contributions from the deep s, p, and d states.....	106
Figure 4.13: The spin-polarized partial density of states (PDOS) of Ru in all tP16-type 3d- $X_3\text{Ru}$ transition compounds ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) was calculated using the GGA functional. The Fermi energy for each compound is set to zero. Additionally, the y-axis of the Ru PDOS has been magnified to better visualize the contributions from the deep s, p, and d states.....	107
Figure 5.1: The calculated lattice constants and density of A15, D0c and tP16 $X_3\text{Ru}$ ($X = \text{Cr and Mn}$) at different pressures. The half-square graphs represent the lattice constants, and the full-squares graphs are for density respectively.....	133
Figure 5.2: Calculated heat of formation as a function of pressure for A15, D0c and tP16 $X_3\text{Ru}$ ($X = \text{Cr and Mn}$) under pressure.....	139
Figure 5.1: Calculated magnetic moments as a function of pressure for A15, D0c and tP16 $X_3\text{Ru}$ ($X = \text{Cr and Mn}$) under pressure.....	140

Figure 5.2: Projected spin polarized density of states for A15 Mn ₃ Ru structures under 0-300 GPa. The Fermi level at 0 eV is represented by a vertical dashed line.....	146
Figure 5.5: Projected spin polarized density of states for A15 Cr ₃ Ru structures under 0-300 GPa. The Fermi level at 0 eV is represented by a vertical dashed.....	147
Figure 5.6: Projected spin polarized density of states for D0c Mn ₃ Ru structures. The Fermi level at 0 eV is represented by a vertical dashed line.....	148
Figure 5.7: Projected spin polarized density of states for D0c Cr ₃ Ru structures. The Fermi level at 0 eV is represented by a vertical dashed line.....	149
Figure 5.8: Projected spin polarized density of states for tP16 Mn ₃ Ru structures. The Fermi level at 0 eV is represented by a vertical dashed line.....	150
Figure 5.9: Projected spin polarized density of states for tP16 Cr ₃ Ru structures. The Fermi level at 0 eV is represented by a vertical dashed line.....	151
Figure 5.3: Pressure dependences of the elastic constants for A15, D0c and tP16 X ₃ Ru (X= Mn and Cr) structures.....	157
Figure 5.4: Dependences of elastic moduli on the pressures for A15, D0c and tP15 X ₃ Ru (X = Mn and Cr) structures.....	163
Figure 5.12: The calculated melting temperature T_m under low- and high-pressure conditions for Mn ₃ Ru and Cr ₃ Ru in A15, D0c and tP16 phases. The brown dotted line represents Ni ₃ Al (1691 K) whilst the green dotted line represents Nb ₃ Al (2333 K).....	169

Chapter One

Introduction

1.1 General introduction

The advancement of transportation on both national and global scales is vital as it plays a crucial role in driving economic activity, facilitating trade, and enabling the exchange of commodities and goods [1]. In the past, people relied on the local markets due to the lack of reliable and safe transport. The availability of transportation in our daily life promotes networking, multiculturalism and industry development. Additionally, it is crucial for research, job creation and economic development both domestically and internationally. A diverse network of transportation services such as vehicles, trains, aircraft, boats, ships, and spacecraft enables the movement of people, materials, machinery and resources across various regions. For instance, in military operations, aircraft are instrumental in transporting essential supplies for workers, medicine and deploying weapons. The evolution of different modes of transportation has captured the interest of both academic and industrial researchers, as these advancements not only enhance national and global income but also elevate the standard of living for populations worldwide [2].

This study contributes to advancements in aerospace transportation, an industry that plays a pivotal role in driving scientific and technological progress while serving as a cornerstone of the global economy. By enabling more sustainable air travel, reducing operational costs, strengthening international trade networks, and expanding employment opportunities, the research bridges materials innovation with tangible economic outcomes. The growing demand for air travel driven by exports, domestic and international connectivity, and the exchange of knowledge across regions has intensified efforts to design new aircraft. Within this context, the development of safe and efficient gas turbine engines remains critical to ensuring both traveler and cargo safety, as well as environmental protection. Aircraft are subjected to stringent regulations locally and internationally aimed at ensuring the safety of travelers and goods as well as protecting the environment. One of the critical factors that directly threatens the safety of the aircraft is the inefficiency of its gas turbine engine [3]. Consequently, growing attention is being directed toward the development of

safe and efficient aircraft gas turbine engines, given their economic and technological significance in determining aircraft safety, operating costs, and environmental impact. Worldwide, governments, industry, and research institutions are investing extensively in advanced propulsion systems, alternative fuels, and optimization strategies to reduce emissions, enhance efficiency, and support the sustainable growth of aviation [4].

The novelty and originality of this work lie in its ability to connect advances in materials science with tangible economic benefits, thereby positioning aerospace research as a driving force for technological innovation and global economic growth.

The efficiency of the gas turbine engines has been compromised over the last few decades due to their operation at elevated temperatures. Notably, turbine blades, one of the most critical components of the gas turbine, are linked to approximately 40% of engine failures [5]. These blades play a vital role in converting thermal energy at high-temperature high-pressure gas into mechanical work [6]. However, while operating in such extreme conditions, the gas turbine blades are vulnerable to oxidation, corrosion, wear and other forms of damage. Such failures can significantly compromise the safety and reliability of turbine engines. Consequently, this study seeks to identify and recommend high-temperature metal alloys suitable for coating turbine blades of gas turbine engines, thereby enhancing their performance in high-temperature structural applications.

1.2 Problem statement

Superalloys are high-performance alloys known for their remarkable tolerance to oxidative environments and extreme temperatures. Typically composed of nickel, iron, or cobalt, these alloys are critical in various high-temperature structural applications. To date, Nickel-based superalloys (NBSAs) are generally used in the hot-section components of gas turbine engines due to their desirable mechanical and structural properties, including high mechanical strength, high melting temperature, relatively low density, good thermal and surface stability, corrosion and surface resistance [7,8].

However, despite the accomplishments of NBSAs, 90% of Ni's melting point has already been exploited [8], limiting their use in the next-generation turbine engines. Hence there is a need to search for alternative alloy systems which can overcome the melting temperature limitation of Ni. Among the materials which have so far been considered for this purpose include Pt, Nb, Cr, Ti and Ru [9–13].

Among these, Ruthenium-based alloys (RBAs) stand out as promising alternatives due to their exceptional mechanical properties, particularly their remarkable resistance to oxidation and corrosion. Notably, the melting point of ruthenium, at 2607.15 K, surpasses those of nickel (1816.15 K), platinum (2045.15 K), and titanium (1941.15 K) [14–16]. When ruthenium is alloyed with platinum and palladium, it makes wear-resistant contacts and resistors. Additionally, Ru is widely utilized as an alloying agent in chemical and electronics industries [17]. It also contributes to the microstructural stability of various material systems [18], while simultaneously improving the mechanical properties and corrosion resistance of titanium, platinum, and nickel-based superalloys, which are critical in jet engine turbine blades [19].

Although a few previous studies have investigated the properties of Ru-based alloys, there remains a significant gap in the literature regarding comprehensive investigations of alloys formed by Ruthenium and 3d transition metals. One of the few recent computational studies employed first-principles approach to investigate the effect of the first row transition metal doping on Cr-Ru alloys [20]. The findings demonstrate that the stability of these alloys, particularly Cr-rich alloys, is enhanced by the presence of transition metals dopants. Based on these findings and considering the remarkable properties of Ru, it is anticipated that transition metal-Ru alloys will exhibit properties that could enhance the efficiency and performance of hot section components of the gas turbine engine. To date no systematic studies on binary transition metals-Ru alloys have been investigated in both computationally and experimentally, indicating a gap that needs to be filled.

To determine the suitability of Ru-based alloys (RBAs) for high-temperature structural applications, it is essential to understand their mechanical and physical properties. This investigation employs quantum mechanical techniques to analyze the structural, electronic,

mechanical, and magnetic properties of Ru-based alloys, specifically $X_3\text{Ru}$ ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) across the A15, D0c and tP16 phases.

1.3 Aims and Objectives

The goal of this research is to model the structural, electronic, magnetic and elastic properties of A15, D0c and tP16-Ru-based alloys $X_3\text{Ru}$ ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn}$) for high-temperature structural applications, using quantum mechanical techniques.

Specific objectives of the study include the following:

1. To calculate the heats of formation of A15, tP16 and D0c $X_3\text{Ru}$ alloys and determine their chemical stability.
2. To determine and analyze the electronic and magnetic properties of A15, tP16 and D0c $X_3\text{Ru}$ alloys.
3. To calculate and analyze the mechanical properties of A15, tP16 and D0c $X_3\text{Ru}$ alloys.
4. To calculate the pressure dependent phase stability of the most stable systems in A15, tP16 and D0c $X_3\text{Ru}$ alloys ($X = \text{Cr and Mn}$) alloys as determined from objectives 1, 2 and 3 above.

1.4 Thesis Outline

Chapter 1 presents a comprehensive overview of the study, including the problem statement, as well as the research aim and objectives.

Chapter 2 provides a literature review that examines previous research in the subject area, with a particular emphasis on nickel-based super alloys. Studies on other alloys such as Ni_3Al [8] are presented, highlighting their benefits and limitations in comparison with conventional NBSAs. Additionally, a critical analysis of previous studies in ruthenium-based alloys is provided, including discussions of its phase diagrams and key material properties.

Chapter 3 describes the theoretical framework and computational methodology employed in this study. It provides the background of quantum mechanical techniques and outlines the Density

Functional Theory (DFT) approach, including its approximations and both pseudopotential and full-potential methods.

Chapter 4 presents the results of the structural stability, electronic and mechanical properties of 3d-transition metal ruthenium-based alloys in the A15, D0c and tP16 crystal phases.

Chapter 5 presents the DFT results for the structural stability, electronic and mechanical properties of $X_3\text{Ru}$ ($X = \text{Cr}, \text{Mn}$) in the A15, D0c and tP16 phases under both fixed and varying pressure conditions.

Chapter 6 finally provides a summary of the key findings and presents the main conclusions drawn from the study.

Chapter Two

Literature review

2.1 Overview

High-temperature materials have attracted considerable research interest due to their critical role in demanding aerospace applications, where components are routinely exposed to extreme thermal, mechanical and environmental conditions. Among these materials, nickel-based superalloys (NBSAs) have become the cornerstone of high-temperature structural applications, particularly in gas turbine engines due to their desirable properties [21–23]. Nevertheless, despite their widespread use, NBSAs exhibit limitations [14] that motivated the exploration of alternative alloy systems capable of advanced material performance.

This chapter provides a comprehensive overview of the main components and operation of a gas turbine engine, with particular emphasis on the high-temperature structural environments encountered by critical components. Understanding these operational demands establishes the material performance requirements necessary for next-generation turbine technologies. In this context, the chapter reviews both experimental and computational investigations of the mechanical properties of a range of materials, including Ni-, Pt-, Nb-, Ti-, Cr-, Ru-based alloys, as well as refractory high-entropy based alloys, for high-temperature structural applications. Furthermore, we discuss the phase diagram of the Cr-Ru alloys which provides the basis of the crystallographic phases considered in the current study. Lastly, the chapter will focus on Ru-based alloys, highlighting their material properties and implications for high-temperature applications.

2.2 Gas turbine engine

A gas turbine (GT) engine, as illustrated in Figure 2.1, is an internal combustion engine that utilizes air for cooling rather than water. The GT unit comprises three key components: a turbine blade (TB), a bar, and a combustor air inlet. In the turbine stage, the TB is positioned directly after the combustor. The primary role of the combustor is to introduce energy into the combustor system

by burning a fuel-air mixture, generating the high-temperature, high-pressure gases required to drive the turbine [24]. Gas turbine engines operate in extreme thermal environments, especially in the combustion chamber and turbine section, where temperatures can exceed 1773.15 K. To survive and perform under these conditions, materials must be resistant to thermal degradation, maintain mechanical strength and withstand corrosion and creep. The combustor typically consists of a ring of fuel injectors that inject a steady stream of fuel into combustion chambers where it mixes with the air. The mixture is burned at temperatures of more than 1366.45 K. The combustion produces a high-temperature, high pressure gas stream that enters and expands through the turbine section. As illustrated in Figure 2.2, turbine blades (TBs) are designed to harness energy from the combustor's high-temperature, high-pressure gas typically features cooling holes to manage heat effectively. An important aspect to be considered in the material engineering of a gas turbine engine is the turbine entry temperature (TET) [25], defined as the point at which the hot gases enter the turbine system. TET is a critical factor governing engine performance and material selection and must be carefully considered during turbine design [26]. As the gas stream moves through the system, its temperature decreases due to energy extraction and mechanical work [27]. In modern aircraft engines, TET can exceed 1800 K during take-off [28].

Components within turbine engines can endure this extreme temperature due to regular air cooling. Over the past 40 years, significant progress has been made in increasing TETs in response to growing demands for power and improved fuel efficiency [29,30]. Moreover, turbine components have been engineered to function at elevated TETs by modifying the metal surface to tolerate higher metal temperatures. This innovation laid the groundwork for the development of thermal barrier coatings (TBCs) [31] to protect the turbine blades from temperature materials. TBC systems are typically composed of high-melting point materials capable of withstanding oxidation and hot corrosion, and as a result protect turbine blades from excessive thermal loads.

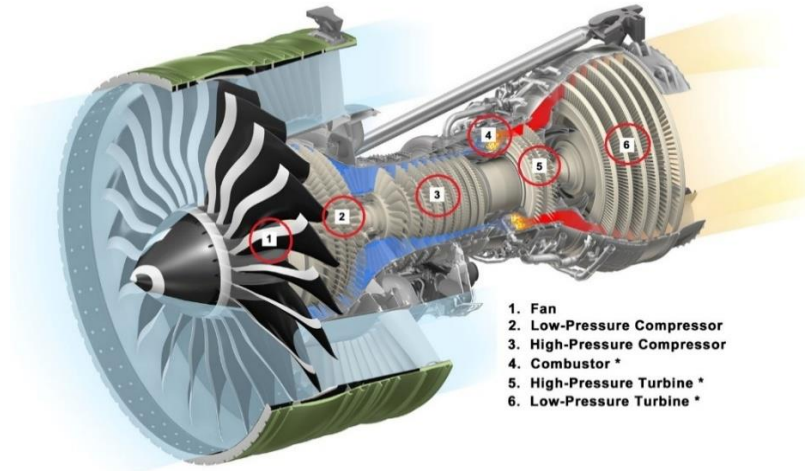


Figure 2.1: Illustration of the main components of the commercial aircraft turbine engine [30,32].



Figure 2.2: Illustration of turbine blade showing holes for cooling [33].

A typical TBC consists of four distinct layers: the ceramic topcoat (CTC), the thermally generated oxide (TGO), bond coat (BC) and the substrate (S). The CTC layer is designed to endure temperature fluctuations due to its low thermal conductivity and insulating properties. The TGO, which forms during the reaction between the BC and CTC at elevated temperatures, is an oxide layer with a thickness ranging from 1 to 10 micrometers. The BC is a metallic layer, typically 75-150 micrometres, thick play an essential role in bonding the CTC to the substrate, and it is made up of materials that have high-melting-point excellent oxidation resistance. Since the turbine blades are continuously subjected to oxidation and hot corrosion [34], the TBC system plays a critical role in extending the lifespan of a commercial turbine engine. During operation, turbine

blades are subjected to various failure mechanisms, including fatigue, creep, corrosion, erosion and sulfidation. Failure of turbine blades can severely compromise the safety and reliability of gas turbine engines, underscoring the need for advanced materials for high-temperature applications.

2.3 High-temperature structural materials

In response to the stringent operating conditions often encountered in gas turbine engines, the development of high-temperature materials has emerged as a solution to address failures commonly encountered in gas turbine engines [14,27,35]. These materials are designed to endure extreme conditions including high-temperatures, high strain and corrosive oxidizing environments.

Nickel-based superalloys (NBSAs) are generally used in hot-section components of the gas turbine engines due to their excellent combination of properties, including good mechanical strength, high melting temperature, relatively low density, thermal and surface stability, and outstanding resistance to corrosion and oxidation [14,36]. Among these materials, Ni_3Al superalloy has attracted attention, and extensive research has been conducted on the system owing to its exceptional mechanical properties compared to other NBSAs. Previous studies have demonstrated that the strength of Ni_3Al is directly proportional to temperature [21], and it exhibits excellent ductility at both room and elevated temperature [22,23]. Furthermore, First-principles calculation [37] predicted that among the Ni_3Al structures cubic $L1_2$, tetragonal $D0_{22}$, and hexagonal $D0_{19}$, the cubic $L1_2$ phase is weakly ferromagnetic, a magnetic moment of $0.71 \mu_B$ and the most stable which agreed with the experimental data [38,39]. Moreover, the electronic property analysis reveals a metallic conductivity as well as a link between structural stability and the density of states at the Fermi level, $N(E_F)$. Specifically, atomic configurations that are more energetically stable exhibit a reduced DOS at the Fermi energy [40]. The temperature-dependent ductility of these alloys is a critical factor for the development of next-generation materials.

Despite significant efforts to enhance temperature capability of NBSAs through complex alloying additions and innovative alloy design methods [41], progress has been limited, with only 373.15 K temperature gain having been achieved over the last two decades. This limitation has motivated

continued exploration of alternative materials capable of operating at high temperatures. Consequently, materials such as Pt-, Nb-, Ti-, Cr-based alloys, as well as refractory high entropy alloys have been investigated as potential candidates for future high-temperature structural applications. Further details on these materials are presented in the following sections.

2.3.1 Pt-based alloys

Platinum-based alloys are earmarked as potential candidates for use in elevated-temperature environments, particularly due to their microstructures and chemistry that are similar to those of Nickel based Super alloys (NBSAs). In addition, Pt has a higher melting point (2045.15 K) than Ni (1816.15 K) and offers improved corrosion resistance compared to NBSAs [42]. Notably, Pt-based alloys can perform effectively at temperatures of up to 1623.15 K [43–45]. Among the Platinum-based alloys, Pt₃Al in L1₂ phase, has been studied experimentally using the arc-melting method [45,46] and it has been found to possess outstanding oxidation resistance. First-principles calculations show Pt₃Al is metallic, with good electron conductivity. Its electronic structure show a sharp DOS peak at the Fermi level (E_f), indicating structural instability that may cause lattice softening that affect both phonons and elastic moduli [47,48]. Further research conducted by Hill et al [46,49,50] has focused on XPt binary alloys and XRhPt (X = Zr, Hf, Rh) ternary alloys. While these alloys demonstrate weaker oxidation resistance, they display remarkably promising mechanical properties.

While platinum-based alloys are unlikely to replace NBSAs on account of their higher cost and density (platinum's density being 21.5 g/cm³ compared to nickel's 8.9 g/cm³), they hold potential for use as coatings in components subjected to extreme temperatures [42,51–53]. Among platinum-based materials, Pt-Al alloys stand out as the most effective high-temperature coatings, finding applications in the advanced gas turbine engine industry [54–58]. Notably, Pt₃Al has a melting point of 1829 K, which is significantly higher than that of Ni₃Al (1372 K) [59].

Recent theoretical and experimental study by Pan [57] indicated that Pt₃Al possesses a tensile fracture strength of 449.5 MPa with good deformation resistance. Additionally, cubic Pt₃Al demonstrates better ductility as opposed to Ni₃Al due to the strength of the Pt-Al metallic bond

[60]. However, Pt-based alloys are presently hindered by their brittleness, weight and cost with low mechanical resistance in high-temperatures [61] limiting their use in high-temperature structural applications. [62]. In addition, the $L1_2$ - Pt_3Al phase is known to transform to unstable phases at low temperatures [63,64]. Significant debate persists regarding the phases present within the Pt_3Al system, and recent work has focused on stabilizing it against unexpected re-ordering [65]. ..Ongoing studies are addressing the above limitations of Pt-based alloys through doping with Ru, Pd, Os, Ir, Au, and Rh [66]. Some research groups are also investigating varying concentrations in Pt–Y and Pt–Sc alloys to identify mechanisms that could enhance ductility [67]. These limitations have prompted investigation into other refractory systems, particularly niobium-based alloys.

2.3.2 Niobium-based alloys

Niobium possesses a melting point of 2740 K, which is significantly higher than that of nickel (1816.15 K) and platinum (2045.15 K) [63,68]. This high melting temperature suggests that NBAs could endure extreme thermal environments more effectively than the nickel-based superalloys (NBSAs) or platinum-based alloys (PBAs). Although the density of niobium (8.57 g/cm³) is much higher than that of Ni (6.84 g/cm³), it is significantly lighter than that of platinum (21.5 g/cm³), which positions niobium as a favorable alternative to platinum in terms of weight. Studies on the phase diagram of binary Nb–Al using the arc-melting method have revealed the presence of Nb_3Al (A15 structure, Cr_3Si type), Nb_2Al (D8b structure, α CrFe type) and $NbAl_3$ (D0₂₂ structure, $TiAl_3$) [69,70]. First-principles calculations under pressure reveal that Nb_2Al exhibits metallic behavior based on density of states results [71]. Similarly, Nb_3Al and Al_3Nb show metallic characteristics under pressure, with enhanced covalency arising from increased hybridization between Nb-4d and Al-3p states [72]. Recent studies on A15-type Nb_3Al conventional superconductors highlight their potential as next-generation high-field magnet materials, owing to superior superconducting properties and reduced strain sensitivity compared to the industrial Nb_3Sn superconductor [73]. However, single-phase Nb_3Al and Nb_2Al exhibit considerable brittleness at room temperature, limiting their use in structural components. As a result, attention shifted toward the refractory high-entropy alloys, which aim to overcome these limitations.

Researchers are actively addressing this limitation by developing strategies to overcome brittleness while preserving high-temperature stability [74]. Notably, computational alloy design has successfully been used to reduce brittleness and enhance mechanical resistance.

2.3.3 Refractory high entropy alloys

To address the limitations associated with Nb, Pt and Ni-based superalloys discussed above, refractory high entropy alloys (RHEAs) based on Mo, Nb, Ta, W, Ti have emerged [75–80] as promising alternatives. Pioneering research by Senkov et al. [81] first identified RHEAs as novel alloy systems suitable for high-temperature applications. These alloys are characterized by their remarkable resistance to wear, erosion, and abrasion, along with the presence of high-strength layers. Refractory high-entropy alloys such as NbMoTaW [82] and AlMo_{0.5}NbTa_{0.5}TiZr [80] exhibit impressive mechanical properties at high-temperatures. Importantly innovative alloys such as Ti_{50-x}Al_xVNbMo [83] have been shown to possess not only high strength, good plasticity, but also significantly reduced density comparable to typical nickel-based superalloys. However, the poor oxidation resistance and relatively low high-temperature strength, along with brittleness, have limited the full potential of RHEAs as high-performance structural materials [79]. Other research groups have confirmed the limitations highlighted above [84,85].

Beyond conventional HEAs, recent studies have explored ultra-HEAs [86], which offer improved ductility, oxidation resistance, and high-temperature stability compared to traditional RHEAs. In addition, novel invar-type alloys [87] with tailored thermal expansion and enhanced oxidation resistance present promising alternatives to brittle RHEAs. Consequently, more conventional lightweight alloy systems, such as titanium-based alloys, continue to be explored for applications where weight reduction is critical. Recently researchers are in an attempt to solve the brittle problem.

2.3.4 Ti- based alloys

Titanium-based alloys are renowned for their strength and lightweight properties, with a relatively low density of 4.5 g/cm³, which is significantly lower than that of Ni (8.9 g/cm³), Pt (21.5 g/cm³) and Nb (8.57 g/cm³). In addition, Ti possesses a good fracture toughness and fatigue strength [88],

with a melting point of 1941.15 K, which is higher than that of nickel (1816.15 K). Additionally, titanium alloys demonstrate superior specific strength and corrosion resistance, remaining effective at temperatures up to 1023.15 K—far exceeding the capabilities of steel and aluminum alloys. Their exceptional high-temperature resistance and significantly reduced weight, approximately half that of most steel alternatives [89–91] make titanium alloys a preferred choice in modern aircraft construction.

Titanium-based alloys are commonly employed in the manufacturing of critical aerospace components, including frames, engine parts, hydraulic pipes, landing gear, track beams, exhaust systems, tail cones, and aircraft pipes. In particular, Ti6Al4V (Ti64) alloy is used in the aerospace sector due to its robust mechanical properties, wide processing temperature range, and excellent weldability [92]. In specialized applications that demand high-temperature resistance, alloys such as Ti-6Al-2Sn-4Zr-2Mo (Ti-6-2-4-2) and Ti-5Al-2Sn-4Mo-2Zr-4Cr (Ti-17) are preferred [92]. The IMI 834 (alpha Ti-5Al-2.5Sn and beta Ti-15Mo-2.6Nb-3Al-0.2Si) and Ti-metal 834 are special titanium alloys and are currently used in turbine engines as pressure compressors due to good creep up to 873.15 K [16]. Despite their advantages, titanium-based alloys present significant challenges in aerospace applications due to machining difficulties, low thermal conductivity, poor oxidation resistance and brittleness. Recent research on these Ti-based alloys [93] has confirmed the limitations of poor oxidation resistance and brittleness discussed above. In addition, some research groups have sought to address the limitations of Ti-based alloys by investigating rolling deformation and solution treatment to refine grain structure, reduce anisotropy, and thereby improve formability while overcoming processing constraints [94]. This has encouraged further exploration of higher-melting point systems, including chromium-based alloys.

2.3.5 Cr based alloys

Chromium based alloys possess remarkable mechanical properties including a high melting point of 2136.15 K which surpasses that of Ni (1816.15 K), Pt (2045.15 K), and Ti (1941.15 K). In addition, Chromium has a density of 7.15 g/cm³ which is lower than Nb (8.57 g/cm³) and Pt (21.5 g/cm³). A significant concentration of chromium enhances the corrosion and oxidation resistance of platinum and ruthenium coatings. It is well established that Cr is widely used as an alloying

agent, especially in industrial applications, due to its ability to form a strong thin protective oxide layer (Cr_2O_3) when exposed to air [16,95].

Cr-based alloys provide lower density, higher thermal conductivity than Ni-based superalloys, excellent oxidation resistance, and cost competitiveness [95–97]. Since Cr-based alloy systems were first explored in the 1940s, it has been recognized that enhancing their strength and ductility is crucial for their practical applications [95,98]. In the 1950s and 1960s, extensive research focused on binary additions to chromium. Although pure chromium is generally considered brittle at room temperature, its ductility remains a subject of debate, as reported ductile-to-brittle transition temperatures (DBTT) range from 177.15 K to 573.15 K, largely influenced by its purity, particularly the nitrogen content [98]. It was observed that the DBTT of chromium is also influenced by its grain structure and surface conditions [99,100]. Furthermore, solute additions not only strengthen chromium but also enhance its ductility. However, their effects are complex, as certain elements can reduce the hardness of chromium at low concentrations due to solution softening [101,102].

Since research on Cr alloys has been limited since the 1980s, chromium-based alloys for high-temperature applications continue to face challenges, particularly in terms of high-temperature strength, room-temperature ductility, and oxidation resistance above 1173.15 K [97]. Drawing inspiration from the γ - γ' microstructure of face-centred cubic (fcc) Ni-based superalloys, known for their outstanding combination of strength, oxidation resistance, and toughness [27], a renewed approach to designing Cr alloys has emerged. Recently, a “bcc-superalloy” design strategy has been proposed to develop alloys with high strength for several body-centred cubic (bcc) metals including Cr [103–105] and other similar metallic systems such as Fe [106,107], W [108], and Ti [109].

These alloys consist of an A2-type disordered bcc matrix (known as the β phase) combined with ordered-bcc intermetallic precipitates (the β' phase), such as B2-type (CsCl structure) NiAl or TiFe, and L2₁-type AlNi_2Ti . Cr–NiAl alloys align with the bcc-superalloy concept and are comparable to the well-established Fe–NiAl ferritic superalloys; however, Cr–NiAl remains an emerging class of materials with only limited data available to date. This design is intended to

enhance the alloys' strength and creep resistance while maintaining their current ductility. Creep tests demonstrated that the inclusion of the NiAl phase markedly improves the creep resistance of Cr compared to unreinforced Cr at 1123.15 K [103].

Recently, Ma et.al [98] investigated the quaternary Cr-superalloys, Cr(Fe)–NiAl, modified through Fe additions using CALculation of PHase Diagram (CALPHAD), a computational technique. It was observed that Fe enhances the solubility of Ni and Al, leading to a higher precipitate volume fraction, as confirmed by experimental results. Furthermore, the alloys exhibit a high compressive yield strength of approximately 320 MPa at 1273.15 K and demonstrate resistance to age softening related to the low coarsening rate. Despite their advantages, Cr-based alloys also exhibit certain limitations, including a ductile-to-brittle transition temperature (DBTT) above room temperature, vulnerability to oxidation at ultra-high-temperatures ($T > 1273.15$ K), nitrogen embrittlement at elevated temperatures, and the inherently weak high-temperature strength of chromium [95,110]. The brittleness in these alloys is attributed to the small number of primary dislocations slip systems in their crystal structure. Studies have shown that the ambient-temperature brittleness of chromium can be significantly reduced by increasing its purity [96,111]. These challenges have stimulated growing interest in ruthenium-based alloys, discussed in the next section.

Although several alloy systems including Ni, Pt, Nb, Ti, Cr and refractory high-entropy based alloys, as discussed above, demonstrate considerable potential for high-temperature applications, various limitations have hindered their full deployment as summarized in Table 2.1. Consequently, the continued search for alternative high-temperature materials to address the challenges posed by traditional metal-based alloys, has increasingly shifted attention toward ruthenium-based alloys (RBAs) as a promising alternative [125–128]. Ruthenium-based alloys (RBAs) are presently under extensive [125,127] investigation due to their appealing combination of surface and mechanical properties, including high melting point, good oxidation and corrosion resistance. Notably, Ruthenium enhances the microstructural stability of various material systems [125].

2.3.6 Ru-based alloys

Table 2.1: Properties, applications and limitations of the metallic based alloys such as nickel, platinum, niobium, titanium and refractory high-entropy alloys.

Metal-based alloys	Properties	Applications	Limitations
Nickel-based alloys (NBSAs)	-Excellent mechanical strength and creep resistance -good surface and phase stability -high oxidation and corrosion resistance -High melting point (1816.15 K) and relatively low density [14,35]	-Chemical processing vessels and heat exchanger -Space components -Blades and vanes in turbine engines - Nuclear reactors [14,35]	-Low melting point in nickel, with 90% of its melting point already exhausted [14]
Platinum-based alloys (PBAs)	-high melting points (2045.15 K) -Thermal stability and thermal shock resistance -Good corrosion and oxidation resistance [112,113]	-Chemical and glass industries -Space technology [112]	-High cost and density in platinum element [34,49,51,114,115]
Niobium-based alloys (NBAs)	- High melting point (2750.15 K) - Good ductility at room temperature and a moderate density [116]	-Hot components of gas turbines [116,117]	-Poor oxidation resistance and low strength at high-temperature conditions above 773.15 K [116,118,119]
Refractory high-entropy alloys (RHEAs)	High strength, good ductility, and high toughness [78–80]	High-temperatures such as aerospace and gas-turbine engines [78,80,120]	-Low strength, poor oxidation resistance and brittleness at high-temperatures [78–80,120]
Titanium-based alloys (TBAs)	-High strength-to-weight ratios, corrosion resistance, and biocompatibility [88,92]	-Aerospace, medical implants and automotive engineering [88,92]	-Difficult to machine, resulting in lower life expectancy and decreased procedure security -Low strength under elevated temperature [121]
Chromium based alloys (CBAs)	-Lower density, higher thermal conductivity than Ni-based superalloys. -Excellent oxidation resistance, and cost competitiveness [98].	-Medical implant -Heavy machinery components [98]	-Pure chromium and chromium-based alloys are brittle and have low ductility at low and high-temperatures -Poor oxidation resistance above 1273.15 K [98,122–124] -CBAs are structurally unstable [98]

With a melting point of 2607.15 K, ruthenium surpasses Ni (1816.15 K), Pt (2045.15 K), Ti (1941.15 K) and Cr (2180.15 K), positioning Ru-based alloys as strong candidates for high-temperature structural applications. While niobium has a higher melting point (2740.15 K) than that of ruthenium, its applicability in high-temperature scenarios is severely limited by poor oxidation resistance and low strength at temperatures above 773.15 K [129,130]. In contrast, ruthenium retains superior chemical stability under oxidizing conditions. Furthermore, the density of ruthenium lies between that of platinum and lighter metals such as niobium, titanium, and chromium, making it a comparatively lighter alternative to platinum while still offering comparable thermal resilience. Collectively, these attributes, including high thermal stability, favorable oxidation behavior and enhanced microstructural stability, underscore the potential of Ru-based alloys as next-generation high-temperature materials. Nevertheless, despite their promising properties, the development of RBAs remains relatively underexplored compared to conventional superalloys, largely due to cost considerations and limited experimental datasets. This gap highlights the importance of theoretical/computational investigations to identify stable Ru-based alloy phases with desirable structural, electronic and mechanical properties.

2.3.7 Pt-Ga, Pt-Al, Pt-Cr and Ru-Cr in L1₂, D0_c, D0'c and tP16 phases

Building on the promise of Ru-based alloys discussed in the previous section, it is important to examine related platinum group intermetallics, as they provide valuable insight into phase stability and structure-property relationships at elevated temperatures. Platinum-group metals (PGMs) present the potential to form outstanding alloys that can endure ultra-high-temperatures, at least 473.15 K above the limits of current Ni-based superalloys. However, unlike Ni₃Al, which has a stable cubic ground state, the high-temperature cubic phase of Pt₃Al undergoes transformations to tetragonal structures at lower temperatures [131,132] making the material brittle [133]. The crystallographic nature of these tetragonal phases remains somewhat unclear in the literature [131,132], highlighting the complexity of phase stability in Pt-based systems.

According to the phase diagram evaluated by McAlister and Kahan [134], the high-temperature cubic cP4-Cu₃Au (L1₂) phase transforms on the Pt-rich side into the tetragonal tP16-Pt₃Ga structure [135] at approximately 1563.15 K. In contrast, Mishima, Oya and Suzuki [132] reported

a sequence of transformations for stoichiometric Pt_3Al , from $L1_2$ phase to the tetragonal $tI16\text{-U}_3\text{Si}$ ($D0c$) structure at 693.15 K [136], followed by a transformation to the tetragonal $tI16\text{-Ir}_3\text{Si}$ ($D0c'$) structure [136] at 403.15 K. All the $tI16\text{-U}_3\text{Si}$ ($D0c$), $tI16\text{-Ir}_3\text{Si}$ ($D0c'$), and $tP16\text{-Pt}_3\text{Ga}$ structures are tetragonal derivatives of the cubic $cP4\text{-Cu}_3\text{Au}$ ($L1_2$) structure type. Prototypical Pt-based superalloys are prone to forming tetragonal Pt_3Al phases at low temperatures, which negatively affect their mechanical properties.

However, the precise crystallography of these phases remains unclear. The assessed Pt–Al phase diagram only indicates the presence of the high-temperature cubic $cP4\text{-Cu}_3\text{Au}$ ($L1_2$) phase and the low-temperature tetragonal $tP16\text{-Pt}_3\text{Ga}$ phase, while the literature also reports two related tetragonal phases, $tI16\text{-U}_3\text{Si}$ ($D0c$) and $tI16\text{-Ir}_3\text{Si}$ ($D0c'$). This uncertainty may stem from the fact that the internal displacement parameters of the $D0c$, $D0c'$, and $tP16$ Pt_3Al phases have not been determined from the X-ray diffraction data [132,135]. Consequently, theoretical methods such as density functional theory (DFT) have become essential tools for resolving these structural uncertainties.

Chauke et al. [60] carried out a detailed investigation of the various $L1_2$ -type Pt_3Al phases using first-principles density functional theory (DFT) calculations. The results showed that the tetragonal $D0c$ structure tends to transform into the cubic $L1_2$ structure because its lowest energy occurs when the internal displacement parameter $u = 0$. Among the remaining three structure types— $L1_2$, $D0c'$, and $tP16$, density functional theory calculations identified the tetragonal $tP16$ (Pt_3Ga prototype) phase as the thermodynamic ground state, owing to its most negative heat of formation. DFT phonon dispersion curves revealed that all three satisfy the criteria for mechanical stability based on their calculated elastic moduli. However, soft phonon modes appear at the Brillouin-zone boundaries, specifically at the R point for the $L1_2$ and $D0c'$ structures, indicating dynamical instability. In contrast, all phonon modes of the $tP16$ lattice are stable, consistent with its designation as the ground-state phase at absolute zero. Building on these insights and motivated by the need to search for new materials capable of replacing or complementing Pt-based alloys, chromium-ruthenium based alloys were investigated, and their phase diagram was studied.

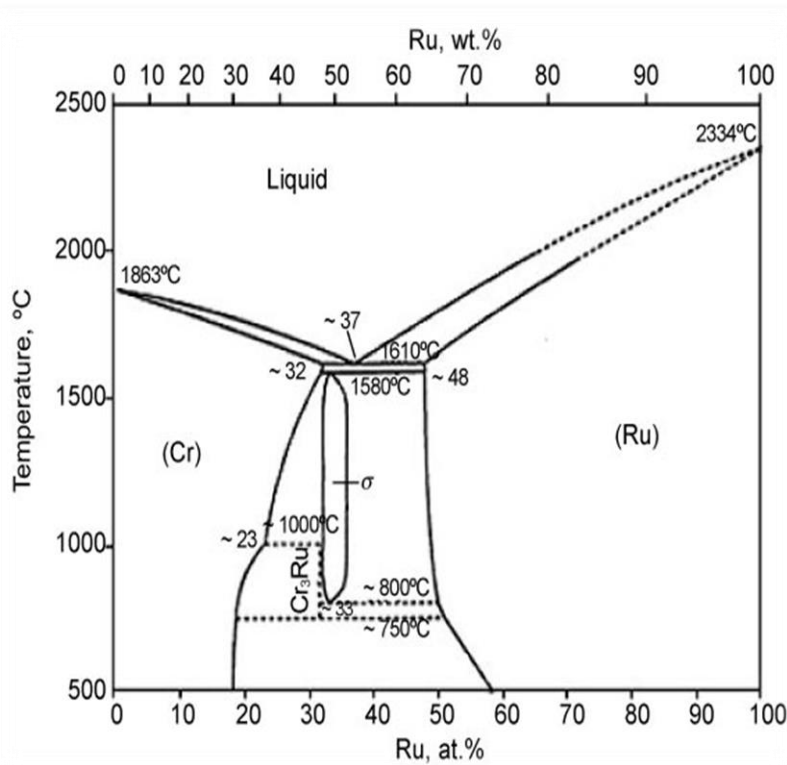


Figure 2.3: Illustration of Cr-Ru phase diagram

The development and optimization of Ru-based alloys are fundamentally guided by the phase diagram of the Cr-Ru system, which provides essential information on phase stability and compositional limits. Phase diagrams are graphical representations that illustrate the various phases of a substance as a function of temperature and composition, showing the conditions under which distinct phases, such as solid, liquid, and gas, exist or coexist [137]. The first experimental study of the Cr–Ru binary phase diagram was conducted by Raub and Mahler [138], later extended by Greenfield and Beck [139]. These researchers identified the terminal solid solutions bcc (Cr) and hcp (Ru), as well as the intermetallic compounds Cr_4Ru , Cr_3Ru , and Cr_2Ru (σ phase), using metallography, X-ray diffraction (XRD) and microhardness testing. Using similar techniques, Savitskii et al. [140] developed the first phase diagram for the Cr–Ru system, incorporating the same phases. Although Raub and Mahler [138] initially proposed the existence of the Cr_4Ru phase, subsequent studies by Shurin and Dmitrieva [141], Wopersnow and Raub [142] and Waterstrat [143] found no supporting evidence on the existence of this phase. In particular, Wopersnow and Raub [142] argued that the diffraction pattern previously attributed to Cr_4Ru by Raub and Mahler

[138] was more likely due to chromium carbide (Cr_7C_3). No experimental thermodynamic data have been reported for the Cr–Ru system. Drawing primarily on the previously mentioned studies, Venkatraman and Neumann [144] evaluated the experimental phase diagram of the Cr–Ru binary system. Cr_3Ru in the A15 phase was reported to exhibit an extremely narrow homogeneity range, justifying its treatment as a stoichiometric compound at 31.5 at% Ru. Similarly, the σ phase was found to possess a relatively narrow homogeneity range, spanning approximately 32 ± 2 to 36 ± 2 at% Ru.

Chevalier and Fischer [145] conducted a thermodynamic optimization of the Cr–Ru binary system using the CALPHAD (CALculation of PHase Diagrams) method [146,147], treating both intermetallic phases (Cr_3Ru and σ) as stoichiometric compounds at 31.5 at% Ru and 33.33 at% Ru, respectively. This approach predicted a homogeneity range of approximately 33 to 34.5 at% Ru, which is narrower than the experimentally determined range reported by Venkatraman and Neumann [144]. The Cr_2Ru heat of formation was computed to be -15000 J/mol, confirming its thermodynamic stability. In addition, the Néel temperature of chromium can be enhanced by increasing the Ru concentration, rising from 311.5 K to 550 K with an addition of approximately 5% Ru. However, this temperature decreases to 273 K when the Ru content reaches 15% [148]. The ternary system results obtained in the present experimental study indicate that the extrapolated solubility of Cr in hcp (Ru) within the binary Cr–Ru system ranges from about 41 at% to 48 at% over the temperature range of 699.8–1473.15 K. These findings highlight the need for re-optimization of the Cr–Ru system to better define both the homogeneity range of the σ phase and the phase boundary of the hcp (Ru) solid solution. More recently, the A15 Cr_3Ru alloy has been synthesized experimentally using various techniques [149]. Resistivity measurements revealed distinct superconducting transitions at critical temperatures $T_c = 2.77$ K for the bcc structure and $T_c = 3.37$ K for the A15 structure, both phases exhibiting high residual resistivity.

Extensive studies on the Pt_3Cr ordered alloy with a Cu_3Au -type structure have clarified its ground-state magnetic properties through tight-binding electronic structure calculations [150]. Spin-polarized band analyses successfully reproduce experimental trends such as local magnetic moments, while the observed ferrimagnetism is attributed to hybridization between Cr 3d and Pt 5d states. Interest in Pt_3Cr remains strong, as A_3B -type intermetallics are valued for their diverse

mechanical, structural, and magnetic characteristics [151,152]. From the Pt–Cr phase diagram [131,153,154], disordered Pt is identified as paramagnetic, whereas Pt₃Cr exhibits strong magnetization [155]. Pt₃Cr is ferromagnetic [156], but its magnetization decreases with increasing Cr content, transitioning to antiferromagnetic behavior near 52 at.% Pt [157,158]. Recent first-principles studies on binary Pt–Ru and Pt–Ir alloys [159] revealed positive heats of formation for both systems (Pt_{100-x}Ir_x and Pt_{100-x}Ru_x), indicating the presence of a miscibility gap at low temperatures. Experimental investigations on Pt–Ir [160,161] and Pt–Ru [131] subsequently confirmed the existence of these miscibility gaps.

Tibane et al. [162] investigated the phase stability of Pt–Cr and Ru–Cr binary alloys in L1₀, B2, L1₂, A15, tP16, D0c, and D0c' structures using first-principles density functional theory. Their results showed that cubic L1₂ Pt₃Cr and A15 PtCr₃ are the most stable, while L1₀ PtCr was more stable than B2. The magnetic moment of L1₂ Pt₃Cr (2.619 μ_B) was found to be consistent with previous experimental value of L1₂ Pt₃Cr (2.52 μ_B) [163] and theoretical of L1₂ Pt₃Cr (2.601 μ_B , 2.623 μ_B and 2.61 μ_B) [164–166] results, validating the reported values for A15 Pt₃Cr (0.001 μ_B), D0c Pt₃Cr (2.690 μ_B), D0'c Pt₃Cr (2.689 μ_B), and tP16 Pt₃Cr (2.726 μ_B). The values indicate that Pt₃Cr in the L1₂, D0c, D0'c, and tP16 structures is magnetic, whereas A15 Pt₃Cr is nonmagnetic. Furthermore, the spin-polarized electronic properties of these phases reveal metallic character. These phases are promising for high-temperature coatings. In contrast, all Ru–Cr compositions exhibited positive heats of formation, indicating thermodynamic instability. All Ru–Cr compositions examined in this study exhibit metallic behavior, with no band gap due to the overlap between valence and conduction bands. Phonon calculations at 0 GPa revealed soft modes at X, Γ , M, and R points for Pt₃Cr A15. While Pt₃Cr L1₂ and PtCr₃ A15 were dynamically stable, RuCr₃ A15 remained dynamically stable but thermodynamically unstable. Phonon density of states analysis identified the atomic contributions to soft modes. These findings point to a general instability in Ru–Cr alloys, thereby motivating further investigation and forming the basis of this present study. Attempts to stabilize the A15 RuCr₃ phase under a pressure range of 0–5 GPa were unsuccessful, as the structure remained unstable throughout. Subsequently, Mnisi BO et al. [167] examined the A15 Ru₃Cr and Cr₃Ru alloys doped with elements such as Mn, Mo, Pt, Pd, Fe, Co, Re, and Zr under zero pressure conditions. These investigations were conducted as part of this doctoral research, with the findings subsequently reported in peer-reviewed publication [167]. The

results demonstrated that Mn doping enhances the thermodynamic stability of these alloys. To date, however, the structural, electronic, and mechanical properties of $X_3\text{Ru}$ (where $X = \text{Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn}$) in the A15, D0c, and tP16 phases have not been comprehensively studied under zero and varying pressure conditions. A detailed examination of these alloys is essential to identify promising candidate materials for diverse applications, particularly in aerospace engineering.

2.4 Physical and structural properties of 3d transition metal elements

Building on the discussion of Ru-Cr alloy stability and the motivation for exploring $X_3\text{Ru}$ alloys, it is important to examine the intrinsic properties of the constituent alloy elements. The alloying behavior and overall performance of Ru-based alloys may strongly be influenced by fundamental physical and structural properties of 3d transition metals. This section reviews the key properties of these elements. The incorporation of 3d-transition metals with Ru-based alloys in this study is primarily motivated by their favorable mechanical [149] and magnetic attributes, particularly evident in Cr, Mn, and Fe. In general, these transition metals possess higher melting points compared to the main group metals [162] and exhibit relatively low densities [167], making them attractive for high-temperature structural applications.

Notable elements such as Ni, Co, Mn, Cu, Ti, Fe, and V are recognized for their ability to enhance the dehydrogenation properties of magnesium hydride [168], improve thermodynamic stability [169] and increase room temperature ductility in various materials [170]. The bonding characteristics in transition metals are influenced by the contributions of both outermost and inner shell electrons [171], resulting in complex electronic interactions that strongly influence their structural and mechanical properties. Consequently, when 3d transition metals form alloys, nitrides, borides or carbides with other metals or elements, they yield durable materials highly sought for a wide range of applications, including high-temperature structural components, catalytic, opto-electronic, and spintronics [169,170,172].

Table 3.2: Physical properties of the 3d transition metals (Ni, Cu, V, Fe, Cr, Mn, Sc, Ti, Co, Zn and Ru)

Element	Space group	Crystal type	Lattice parameter (Å)	Melting temperature (T _m)	Fractional coordinates	Coordination number	Packing factor
Ni	Fm-3m	FCC	3.52	1816.15 K	(0,0,0)	12	0.74 [14]
Cu	Fm-3m	FCC	3.61	1358.15 K	(0,0,0)	12	0.74 [14]
V	Im-3m	BCC	3.03	2183.15 K	(0,0,0)	8	0.68
Fe	Im-3m	BCC	2.87	1811.15 K	(0,0,0)	8	0.68
Cr	Im-3m	BCC	2.884	2180.15 K	(0,0,0)	8	0.68
Mn	Im-3m	BCC	2.79	1519.15 K	(0,0,0)	8	0.68
Sc	P63/mmc	HCP	3.31	1814.15 K	(1/3,2/3,1/4)	12	0.74
Ti	P63/mmc	HCP	2.95	1941.15 K	(1/3,2/3,1/4)	12	0.74
Co	P63/mmc	HCP	2.51	1768.15 K	(0,0,0), (1/3,2/3,1/4)	12	0.74
Zn	P63/mmc	HCP	2.66	693.15 K	(1/3,2/3,1/4)	12	0.74
Ru	P63/mmc	HCP	2.71	2607.15 K	(1/3,2/3,1/4)	12	0.74

Table 2.2 summarizes the physical and structural properties of the 3d transition metals. Table 2.2 presents the crystallographic and physical parameters of 3d transition metals (Ni, Cu, V, Fe, Cr, Mn, Sc, Ti, Co, Zn and Ru), including space group, crystal type, lattice parameters, coordination numbers and melting temperatures. These parameters provide essential insight into atomic packing, bonding characteristics and thermal stability, all of which play a critical role in determining alloy phase stability and performance in high-temperature environments.

2.5 Structural properties of A15, D0c and tP16 crystallographic phases

2.5.1 A15 phase

The A15 phase is characterized as a series of intermetallic compounds that conform to the general formula M_3G , where M is typically a transition metal and G represents another metallic or metalloid element. In the present study, X_3Ru ($X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn$) alloys crystallize in the A15 phase with space group Pm-3N (number 223) and a theoretical lattice

parameter of $a = b = c = 4.63 \text{ \AA}$. The A15 unit cells is illustrated in Figure 2.4, one notable feature of A15 crystal structures is the arrangement of transition metal atoms M, which are positioned such that they form mutually orthogonal and linear chains that exhibit considerable flexibility within the crystal lattice. This configuration contributes to the robustness of A15 structures, which are densely packed and are influenced by the dimensions of the unit cell [173]. In the specific case of $X_3\text{Ru}$ systems, Ru atoms occupy the corners and body centre of the cubic lattice, while the X atoms are organized in pairs on the faces of the cube, as summarized in Table 2.2. This arrangement not only highlights the structural complexity of $X_3\text{Ru}$ but also underscores the intricate interplay between atomic positioning and crystallographic properties inherent in A15 intermetallic.

2.5.2 D0c phase

The $X_3\text{Ru}$ ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu}$ and Zn) crystallize in a body centered tetragonal D0c structure, as illustrated in Figure 2.4. The phase is characterized by lattice parameters of approximately $a=b = 5.225 \text{ \AA}$ and $c = 7.418 \text{ \AA}$. Within the unit cell, Ru atom occupies the 4a crystallographic site, whilst X1 and X2 occupy the 4b and 8h positions as shown in Table 2.3 below, resulting in a total of 16 atoms (12X and 4Ru) per unit cell. The tetragonal distortion in the D0c phase introduces anisotropy in bonding and elastic behavior, which can significantly influence mechanical stability and electronic structure.

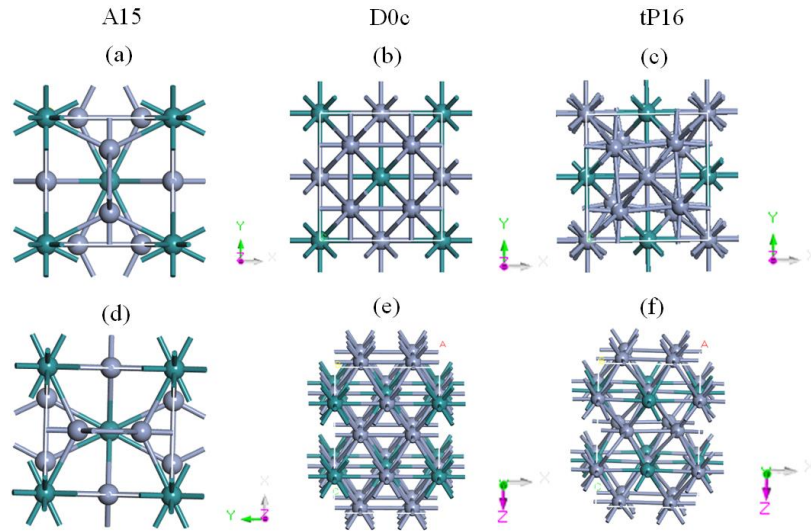


Figure 2.4: Ball and stick illustration of different crystal structure phases of X-Ru alloys. Green balls represent $X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn}$ atoms; Blue balls represent Ru-atoms.

2.5.3 tP16 phase

The tP16 (Pt₃Ga-type) phase is characterized by a tetragonal crystal structure. The unit cell is displayed in Figure 2.4. Similar to the D0c phase in 2.5.2, the unit cell contains a similar number of atoms (16) although their spatial arrangement within the crystal lattice differs, as detailed in table 2.3. leading to distinct structural and electronic characteristics. The experimental lattice parameters for tP16 are approximately $a = 5.459 \text{ \AA}$ and $c = 7.806 \text{ \AA}$. This structure is associated with the prototype (Pt₃Ga) and is classified under the space group P4/mbm. The structural similarities and differences among the A15, D0c and tP16 phases provide a useful framework for evaluating phase stability and structure-property relationships in X₃Ru alloys. The structural similarities and differences among the A15, D0c, and tP16 phases provide a critical framework for evaluating phase stability and structure–property relationships in X₃Ru alloys. In addition, they also determine the suitability of these alloys for high-temperature applications such as gas turbine engines. Thus, examining these phases is essential for linking fundamental materials science to practical performance outcomes.

2.6 Conclusion

This chapter has presented an overview on the structural, electronic, magnetic, and mechanical properties of Ru-based alloys, with particular emphasis on X₃Ru alloys (where X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) across various crystallographic phases including A15, D0c, and tP16, using density functional theory electronic structure methods. Ruthenium is a chemically inert element, which plays a significant role as an alloying agent in the chemical, advanced structural and electronic industries. The focus on 3d-transition metals stems from their favorable combination of high melting points, moderate densities and versatile bonding properties which are essential for materials operating in extreme environments such as gas turbine engines. The research aims to explore the potential of these Ru-based binary alloys to exhibit melting temperatures above 1273.15 K, positioning them as viable alternatives to traditional Ni-based superalloys. Current investigations into these transition metal-Ru alloys are limited in literature, highlighting the need for detailed studies on their structural, mechanical, and electronic properties.

Table 2.3: The atomic positions in the A15, D0c and tP16 X₃Ru (X = Sc-Zn). Where “u” is the displacement parameter.

Structure	Atoms	Locations	X	Y	Z
A15 X ₃ Ru	Ru	1a	0	0	0
	X	3a	0.25	0	0.5
D0c X ₃ Ru	Ru	4a	0	0	0.25
	X1	4b	0.25	0	0.5
	X2	8h	0.25-u	0.75-u	0.00
tP16 X ₃ Ru	Ru	5L	0.00	0.50	0.258
	X1	5M	0.00	0.00	0.251
	X2	5N	0.231	0.731	0.00
	X3	5O	0.290	0.790	0.50

The outcome of this thesis contributes valuable insight into phase stability and suggests new transition metal based –Ru superalloys that surpass the performance of the existing Ni and Pt - based alloys in high-temperature structural applications. Such advancements could contribute to environmentally friendly technologies and improved fuel efficiency. Additionally, the research may extend the applicability of these alloys into fields such as spintronics, optics, magneto-electronics and optoelectronics underscoring their versatility, potential and broader scientific and technological relevance of Ru-based alloy development.

Chapter Three

Computational methodology

Quantum mechanical techniques play an important role in studying the properties of many-body interacting systems using computational simulations. This approach offers a robust means of explaining the properties of material systems with sufficient accuracy, particularly when experimental data is lacking. In this chapter, we will outline the first-principles quantum mechanical framework used in this study.

3.1 The many-body problem

The electronic structure of matter is described by the non-relativistic Schrödinger equation, which governs the behavior of a many-body electronic wave function, $\Psi(r_1, r_2, \dots, r_n)$. The time-independent non-relativistic Hamiltonian of such a system consisting of interacting electrons and nuclei is given as:

$$H_{ele-nuc} = T_{ele} + T_{nuc} + V_{ele-nuc} + V_{ele-ele} + V_{nuc-nuc} \quad (3.1)$$

where

$$T_{ele} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{R}_i}^2}{M_i} \text{ is the kinetic energy operator of the electrons}$$

$$T_{nuc} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_{\vec{r}_i}^2}{m_e} \text{ are the kinetic energy operators of the nuclei}$$

$$V_{nuc-ele} = \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \text{ is the potential energy operators of the electron-nuclei interaction}$$

$V_{ele-ele} = \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$ is the potential energy operators of the electron-electron interaction

$V_{ele-nuc} = -\frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|}$ is the potential energy operators of the nuclei-nuclei interaction

where R_i and r_i are the locations of the nuclei and electrons in i, j states. M_i and m_e relate to the mass of both nuclei and electrons, respectively. The electron-nuclei, electron-electron and nuclei-nuclei interactions defined above arise from Coulomb interactions.

Equation (3.1) can only be solved analytically for a system consisting of a few atoms. However, for a very large number of atoms ($N \sim 10^{23}$) it is intractable to solve; hence, a number of approximations are needed to find its exact solution. The first level of approximation is the Born and Oppenheimer approximation [174]. This approximation disregards the movement of the atomic nuclei when describing the electrons in a molecule. This is due to the significant mass difference between the nuclei and electrons, which makes the nuclei appear stationary compared to the electrons. The consequence of the Born-Oppenheimer approximation is that the electron motion is decoupled from that of heavier ions, setting the kinetic energy operator of the nuclei to zero, while the potential energy operator becomes a constant. Thus, the Born and Oppenheimer approximation reduces the complexity of equation 3.1 to

$$H_{ele-nuc} = T_{ele} + V_{ele-nuc} + V_{ele-ele} \quad (3.2)$$

To solve equation 3.2, the last two terms need to be known: $V_{ele-ele}$ and $V_{ele-nuc}$. Quantum mechanical techniques, such as density functional theory and the Hartree-Fock approximation, are used to determine the accurate equilibrium energy of a material system composed of electrons and nuclei. These methods allow for the calculation of various parameters related to the total energy of the system. This is possible if the exact forms of the right-hand side (RHS) terms of equation 3.2 are known. However, all the terms are known but the exchange correlation energy of interacting electrons remains unknown. The density functional theory accounts for the electron exchange

correlation (Exc) effect for many interacting particle systems, whilst the Hatree-Fork (HF) approach treats the electron exchange accurately but ignores the correlation effects. Hence, the HF approximation cannot accurately predict the properties of metallic and magnetic systems. Moreover, the long-range Coulomb interaction produces an unreasonable depiction of eigenvalues near the Fermi energy in HF.

3.2 Density Functional Theory

The fundamental idea of the Density Functional Theory (DFT) is that any property of a system with many interacting particles can be considered a functional of its ground state charge density. For a system of interacting electrons, DFT asserts that the total energy (E) of the interacting electrons in an external potential, $V_{ext}(r)$, is precisely described as a functional of the system's ground state density $\rho(r)$ [175] given as:

$$E = E[\rho(r)] \quad (3.3)$$

DFT is established from the Hohenberg-Kohn theory [176], which expresses a balanced correspondence among the electron density $\rho(r)$ of a many-electron interacting system and the outer potential V_{ext} imposed by the nucleus. Thus, the accurate ground state wave function is obtained from the outer potential expression due to a correct ground state electron density. Therefore, the minimum energy can be expressed as:

$$E[\rho(r)] = T_{ele}[\rho(r)] + F_{HK}[\rho(r)] + V_{ext}[\rho(r)] \quad (3.4)$$

where, $F_{HK}[\rho(r)]$ is the universal functional of the electron density due to kinetic energy $T_{ele}[\rho(r)]$ and potential interactions $V_{ele-ele}[\rho(r)]$. This universal functional is called the Hohenberg-Kohn density functional and can be described in terms of the interaction between the electron-exchange and correlation and Hartree potential V_H due to classical electrostatic interactions [177] as:

$$F_{HK}[\rho(r)] = T_{ele}[\rho(r)] + \int \frac{\rho(r')}{|r-r'|} dr' + V_{xc}[\rho(r)] \quad (3.5)$$

where, the first term is the kinetic energy of the non-interacting electron system, the second term is the Hartree potential V_H and the third term is the exchange-correlation potential due to electron-nuclei interactions. Now the total energy can be written as:

$$E[\rho(r)] = T_{ele}[\rho(r)] + \int \frac{\rho(r')}{|r-r'|} dr' + V_{xc}[\rho(r)] + V_{ext}[\rho(r)] \quad (3.6)$$

where, the last two terms are external potentials that are split into two categories namely: classical and non-classical energies due to the nuclei $V_{ext}(r)$ and exchange-correlation effects $V_{xc}(r)$. This equation (3.6) can be transformed to:

$$H_{KS}\psi_i = \left(-\frac{\hbar^2}{2m_e} \nabla^2 + \int \frac{\rho(r')}{|r-r'|} dr' + V_{ext}(r) + V_{xc}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r) \quad (3.7)$$

representing the Kohn-Sham energy equation for non-interacting particles. Equation 3.7 effectively minimizes the difficulty of strong electron-nuclei and electron-electron interactions in many-body systems, by mapping them to a single particle moving in an effective potential [176] due to the nucleus. This effective potential is not explicitly known yet can be approximated. The Kohn-Sham equations transform the many-body interacting particle into a single independent particle equation as a functional of an equilibrium charge density, where ψ_i is the single particle Kohn-Sham wave function. Therefore, the ground state density can be described as

$$\rho(r) = \sum_{i=1}^N |\psi_i|^2 \quad (3.8)$$

whilst the exchange-correlation potential, $V_{xc}(r)$ is given by the functional derivative of the ground state total energy with respect to the ground state charge density:

$$V_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \quad (3.9)$$

3.3 The Exchange-Correlation Functional

While the density functional theory (DFT) in principle is an accurate theory describing ground state interactions in a many-particle system, in practice, approximations are needed to describe the electronic exchange correlation term in the Kohn-Sham equation (3.7). Therefore, the effectiveness of DFT depends heavily on the accuracy and reliability of the approximations utilized to the exchange correlation potential, V_{xc} . Consequently, to provide a numerical solution to the Kohn-Sham equations, a number of exchange-correlation functionals have been developed, including the local density approximation (LDA), generalized gradient approximation (GGA), and other hybrid functionals, as illustrated in Figure 3.1.

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + \underbrace{\frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{\text{Coulomb potential}} + V_{ext} + \underbrace{V_{xc}}_{\text{Exchange-Correlation potential}} \right] \psi(\vec{r}) = \epsilon \psi(\vec{r})$$

All electron Full potential ←
 Pseudopotential ←

→ LDA
 → LSDA
 → GGA
 → GGA + U
 → Hybrid functional i.e
 PBE0, B3LYP, Sx-LDA

Figure 3.1: Kohn-Sham-DFT equation and its implementation

3.3.1 Local Density Approximation

The simplest approximation to the exchange-correlation term in the Kohn-Sham equations is the Local Density Approximation (LDA) [178]. LDA assumes the density of a homogeneous electron gas with a gradually changing electron density gradient, for the exchange correlation functional, expressed as [179].

$$E_{xc}^{LDA}[\rho] = \int \rho(r) \varepsilon_{xc}(\rho(r)) dr \quad (3.10)$$

where, ε_{xc} is the exchange-correlation energy per electron in a homogeneous electron gas (HEG).

For simple materials such as metals or an isolated atom, as well as a wide range of material systems, LDA yields reliable results. This is largely due to LDA's effectiveness in approximating the exchange and correlation effects for certain material densities, where these effects are typically short-ranged. However, one notable limitation of the LDA is its inability to account for inhomogeneities in electron density. As a result, it tends to overestimate bonding energies in both molecular and solid systems.

For magnetic systems, the total energy of the system is calculated by incorporating spin polarization into the exchange correlation term. This gives rise to the local spin density approximation (LSDA). Thus equation (3.10) can be written as:

$$E_{xc}^{LSDA}[\rho] = \int \rho(r) \varepsilon_{xc}(\rho_{\alpha}(r), \rho_{\beta}(r)) dr \quad (3.11)$$

where the charge density comprises of spin up α and down β densities:

$$\rho(r) = \rho_{\alpha}(r) + \rho_{\beta}(r) \quad (3.12)$$

In a spin-polarized system, the total energy expression from Equation 3.3 is reformulated as a functional dependent on both the ground-state spin-up and spin-down electron densities.

$$E = E[\rho_\alpha(r), \rho_\beta(r)] \rho_\alpha(r) \quad (3.13)$$

This modification to the Kohn-Sham equation (Equation 3.7) introduces an additional term $\pm \mu_B B_{xc}(r)$ that accounts for the ground-state magnetization of the electron system. In this context, $\mu_B = e\hbar / 2mc$ denotes the Bohr magneton, and B_{xc} represents the magnetic exchange field experienced by an electron. Consequently, the Kohn-Sham equation for spin-polarized systems is reformulated to incorporate this magnetization-dependent contribution.

$$H_{KS} \psi_i = \left(-\frac{\hbar^2}{2m_e} \nabla^2 + \int \frac{\rho(r')}{|r-r'|} dr' + V_{ext}(r) + V_{xc}(r) - \mu_B B_{xc}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r) \quad (3.14)$$

where the charge density defined by Equation (3.8) is decomposed into spin-up and spin down densities corresponding to different sets of the Kohn-Sham orbitals:

$$\rho_\alpha(r) = \sum_{i=1}^N |\psi_i^\alpha|^2 \quad (3.15 \text{ a})$$

$$\rho_\beta(r) = \sum_{i=1}^N |\psi_i^\beta|^2 \quad (3.15 \text{ b})$$

Thus, in a spin-polarized system, the total energy is formulated as a functional of the spin-up and spin-down charge densities $\rho(r) = \rho_\alpha(r) - \rho_\beta(r)$. The resulting spin density arising from spin polarization is defined as $M = \int (\rho_\alpha(r) + \rho_\beta(r)) dr^3$, and the total magnetic moment (M) can be derived from this quantity given as:

$$M = \int (\rho_\alpha(r) - \rho_\beta(r)) dr^3 \quad (3.16)$$

Calculating the properties of a spin-polarized many-body system necessitates a two-dimensional spin space, which in turn demands sampling a larger portion of the Brillouin zone. In practical terms, spin-polarized calculations are carried out independently for spin-up and spin-down

components, requiring increased computational effort to achieve convergence, as both the standard $\rho_\alpha(r) + \rho_\beta(r)$ and the spin charge density $\rho_\alpha(r) - \rho_\beta(r)$ must be converged separately.

Due to the extra degrees of freedom introduced by spin density, spin-polarized Kohn-Sham equations can yield multiple metastable self-consistent solutions, each reflecting a different spin configuration. Identifying the true ground state and ensuring no possible solutions are overlooked, a comprehensive and computationally demanding search is needed [180].

Because the energy differences between metastable spin configurations are often minimal, self-consistent field (SCF) calculations may converge to a nearby metastable state, potentially overlooking other solutions if all spin configurations are not thoroughly explored [181]. To address this, the Fixed Spin Moment [182] (FSM) method as a constrained DFT approach can streamline the search for the true magnetic ground state. However, verifying whether a given spin configuration represents a true local minimum requires follow-up calculations using Unrestricted Spin Optimization (USO). Both methods were employed in this work, with various initial spin and geometry configurations, to reliably identify the ground state and relevant metastable spin states, where a well converged Hubbard U of 2.5 eV was applied for all the studied compounds.

Magnetic ordering in solids arises from a balance between kinetic energy and exchange-correlation effects [180]. While parallel spin alignment lowers exchange energy, it increases kinetic energy due to valence electron delocalization making most solids non-magnetic. Magnetism emerges only when electrons are sufficiently localized, as seen in elemental ferromagnets such as Cobalt and Iron [183].

3.3.2 Generalized Gradient Approximation

The Generalized Gradient Approximation (GGA) functional is an improvement over the LDA, by taking into account the gradient of the electron density $|\nabla\rho|$ as well as its magnitude at each point r . This functional allows better description of inhomogeneous systems compared to LSDA. Consequently, the total energy of the system can be expressed as

$$E_{xc}^{GGA}[\rho] = \int \rho(r) \varepsilon_{xc}(\rho(r), |\nabla \rho(r)|) dr \quad (3.17)$$

The GGA is derived from the gradient expansion approximation (GEA) based on LSDA. In this framework, electrons are accounted for in a homogeneous system. Inclusion of information on the electron density spatial variation in GGA results in greater flexibility in describing real materials. However, GGA is inadequate in describing the behaviour of low densities as well as describing the properties of strongly correlated material systems, such as transition metal oxides and some magnetic systems.

3.3.3 Generalized Gradient Approximation with the Hubbard Parameter (GGA + U)

To improve the accuracy of GGA an additional term called the “Hubbard U parameter” is used to effectively treat the delocalised and localised orbitals with strong on-site coulomb interactions [184]. This necessity arises from the absence of correlation between unpaired d and f electrons in such material systems, highlighting the need for electron correlation [185]. To address this limitation in GGA, the Hubbard model, along with an onsite term, is incorporated into the Hamiltonian of the wave function, as [186,187]:

$$H = B \sum_{\langle i,j \rangle} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3.18)$$

where B is the hopping term, U is the onsite Coulomb repulsion, $\langle i, j \rangle$ taken as the nearest neighbour lattice site, $c_{i\sigma}^{\dagger}$ and $c_{j\sigma}$ are construction and the destruction operators for a spin σ in the i^{th} lattice site respectively. The Hubbard U parameter is usually obtained semi empirically but can also be extracted from ab initio calculations. However, both methods do not permit the transferability of U across compounds.

While the GGA + U functional has demonstrated to be robust in some strongly correlated systems, there are more accurate non-local hybrid functionals available, such as B3YLP [188], HSE03 [189] and Sx-LDA [190]. However, these functionals are computationally intensive and as such are

typically feasible only for small systems. Therefore, in this study, we employ the GGA+U functional due to its balance of accuracy and relatively low computational cost compared to non-local hybrid functionals.

3.4 The Hartree Potential

There are two primary approaches for solving the Hartree Potential in the Kohn-Sham equation: the full potential approach and the pseudopotential approach. The full potential approach treats all core and valence electrons equally within the framework of density functional theory (DFT). In contrast, the pseudopotential approach considers only the valence electrons [191], effectively simplifying the calculations by approximating the influence of the core electrons. In this section, we will provide a brief overview of both approaches, placing more emphasis on the pseudopotential technique, which has been adopted in this study.

3.4.1 Full potential approach

Full Potential Plane Wave (FP-PW) methods are among the most accurate techniques for solving the Kohn-Sham equations. These methods account for all electrons within an atom, including core electrons, where the potential and wave functions exhibit significant variation. Consequently, FP-PW methods can reliably determine material properties that depend on the behaviour core electrons, such as core electron polarization and hyperfine interactions. The FP-PW method offers several advantages, including a reduction in the number of plane waves needed, accurate evaluation of matrix elements, reliable estimation of absolute total energy, and efficient use of computational resources. However, despite its successes, FP-PW methods are relatively slow to converge in the core region of the atom, achieving high numerical accuracy can prove challenging, with the most notable drawback being the basis-set superposition error [192]. This error may be estimated but cannot be fully addressed unless a more comprehensive basis is used.

3.4.2 Pseudopotential approach

The pseudopotential approach presents the most effective strategy for reliably describing the rapidly varying functions within the core region of atoms. This method typically involves "freezing" the core electronic states and reformulating the governing wave function to accommodate the smoother pseudo-wave functions of valence electrons, as illustrated in Figure 3.2. In contrast to the full potential technique, pseudopotential methods are based on the fact that core states are not necessarily essential for the description of chemical bonding, and therefore a good description of the valence wave functions inside the core region is not strictly required since core states are highly localized and are not involved in chemical bonding. Therefore, if the solution inside some cut-off radius between the core and valence region is replaced with a smooth wave function (called pseudo wave function), then there will be no loss of information in describing those properties of materials (e.g. chemical interaction) which are primarily dependent on the valence electrons. This allows the electronic wave function to be expanded using a much smaller number of plane wave basis sets, thus minimizing the computational cost, compared to full potential plane wave methods. However pseudopotential methods are inefficient in obtaining information that is inherently contained in the region near the nucleus (e.g. hyperfine fields and polarization at the core) [193]. Although full potential methods have superior accuracy, pseudopotential techniques have become increasingly popular and have been found to maintain good accuracy for a wide variety of materials [194]. The results reported in this thesis have been obtained using ab initio DFT pseudopotential methods.

3.4.2.1 Norm-conserving Pseudopotentials

The fundamental principle of norm-conserving pseudopotential [195,196] is that the pseudo-charge densities must match the true charge densities outside the core region in order to satisfy the orthogonality condition [195,196]. This requirement is called norm-conservation, and it guarantees that the pseudopotential is useful, not only in every energy range, but also in all environments such that its eigenvalues do not depart significantly from those used in its construction.

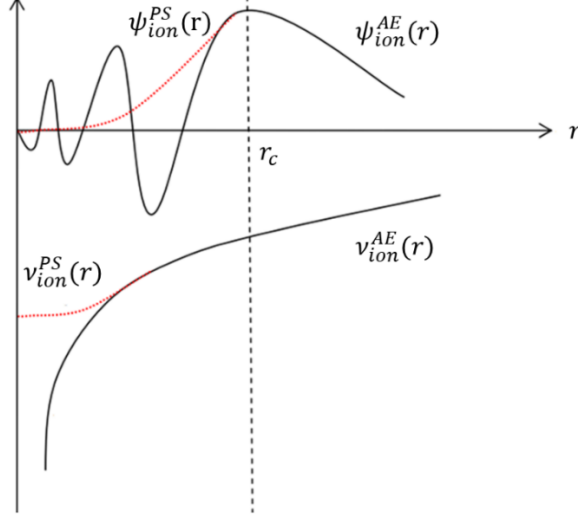


Figure 3.2: Schematic delineation of the pseudo-potential model. The dense lines display the all-electron wave-function, $\psi^{AE}(r)$, and ionic potential, $v_{ion}^{AE}(r)$, while the dashed lines show the relating pseudo-wave-function, $\psi^{PS}(r)$, given by the pseudo potential, $v_{ion}^{PS}(r)$. All quantities appeared as a function of distance, r , from the atomic nucleus [197].

Typically, the generation of norm-conserving pseudopotential involves creating a node-free pseudo-wave function that aligns with the all-electron wave function at core radius, with a specified level of continuity, followed by inverting the radial Schrödinger equation. To achieve a norm-conserving pseudopotential, four key requirements must be met, which are outlined as follows:

- (1) The valence pseudo $\psi_i^{PS}(r)$ and all electron $\psi_i^{AE}(r)$ wave functions should be similar outside a given cut-off radius r_c .
- (2) The two wave functions must have equal charge enclosed within r_c .

$$\int_0^{r_c} |\psi_i^{PS}(r)|^2 dr = \int_0^{r_c} |\psi_i^{AE}(r)|^2 dr \quad (3.19)$$

and can be normalized such that $\int_0^{r_c} |\psi_i^{PS}(r)|^2 dr = \int_0^{r_c} |\psi_i^{AE}(r)|^2 dr = 1$ hence, this is known as the norm conservation.

(3) The $\psi_i^{PS}(r)$ must be continuous at r_c , have zero nodes and its first and second derivatives respectively.

(4) The eigenvalues must be equivalent for both valence electron and pseudo-potential.

All these conditions permit freedom when generating a pseudo-wave function and constructing pseudo-potentials. The pseudo-potential is constructed based on the radial Schrödinger wave function equation as:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + v_H(r) + v_{xc}(r) \right] * \psi_l^{AE}(r) = \epsilon_l \psi_l^{AE}(r) \quad (3.20)$$

where $v_H(r)$ and $v_{xc}(r)$ are Hartree and exchange-correlation potential at a distance r , and $\psi_l^{AE}(r)$ is the all electron wave function with angular momentum component l . Equation (3.20) should be inverted to obtain the ionic pseudo-potential once the pseudo-potential had been generated, giving

$$v_{ion,l}^{PS}(r) = \epsilon_l - v_H^{PS}(r) - \frac{l(l+1)}{2r^2} + \frac{1}{2\psi_l^{PS}(r)} \frac{d^2}{dr^2} \psi_l^{PS}(r) \quad (3.21)$$

However, for each angular momentum component l , there should be a separate pseudo-potential. Pseudo-potentials such as (3.22) are called non-local norm conserving pseudo-potential and can describe the core ion scattering in a range of surroundings. To find great flexibility in the generation of pseudo-potential wave function, equation (3.21) should be relaxed. This scheme involves the partitioning of total valence density $\rho(r)$ into hard and soft contribution giving:

$$\rho(r) = \sum_n \left[|\varphi_n(r)|^2 + \sum_j \langle \beta_j | \varphi_n \rangle \right] \quad (3.22)$$

where β_i are projector functions depending on the ionic locations, and the augmentation function is given by $Q_{ij}(r)$ below as:

$$Q_{ij}(r) = \psi_i^*(r)\psi_j(r) - \phi_i^*(r)\phi_j(r) \quad (3.23)$$

where $\psi_i(r)$ and $\phi_i(r)$ are the all-electron wave functions and ultra-soft wave functions. The orthogonality condition of the wave functions gives:

$$\langle \phi_i | M(\{R_I\}) | \phi_j \rangle = \varepsilon_{ij} \quad (3.24)$$

where $M(R_I)$ depends on the ionic position through $|\beta_i\rangle$ and it is given by:

$$M = 1 + \sum_{i,j} q_{ij} |\beta_i\rangle \langle \beta_j| \quad (3.25)$$

$$\text{and } q_{ij} = \int Q_{ij}(r) dr \quad (3.26)$$

Norm conserving pseudopotentials generally require a large number of plane waves to converge; hence they are computationally expensive. In addition, it has been observed that the norm-conserving pseudo-potential can provide inaccurate descriptions of transition metals [198] due to their highly localized valence atomic orbitals. This makes the norm-conserving pseudo-potential problematic for representing the pseudo-wave function in a plane wave basis. Transition metals require a large basis set to describe the properties accurately. This forces the pseudo-wave function to vary quickly due to norm conserving criteria. Since this is not feasible, the only option is to increase the core radius, which negatively affect the transferability and quality of the pseudo-potential. To address the limitations of norm conserving pseudopotential, alternative pseudo-potentials called "ultra-soft" pseudo-potentials [199] have been developed.

3.4.2.2 Ultrasoft-Pseudopotentials

Ultrasoft Pseudopotentials (USP) [53] relax the norm conservation condition associated with norm conserving pseudopotentials. This is achieved by imposing a transformation that redefines the problem in terms of a smooth function and an auxiliary function around each core. This approach allows calculations to be performed with the lowest possible cut-off energy for the expansion of

the plane wave basis set. As a result, it enhances the transferability of the pseudopotentials even for large cut-off radius. In general, ultra-soft pseudo-potentials results in a smoother pseudo-wavefunction compared to norm conserving pseudo-potentials. Thus, it uses fewer plane-waves for the calculation of the total energy of the system at equivalent accuracy, yielding results that are comparable to those obtained with full potential methods [200]. For this reason, the ultra-soft pseudo-potential are employed throughout this study.

In constructing ultra-soft pseudopotentials, the norm-conservation constraint (Equation 3.19) is relaxed, providing greater flexibility in constructing the pseudo-wave functions. In this approach, the total valence density $n(r)$ is divided into hard and soft contributions as.

$$n(r) = \sum_n |\phi_n(r)|^2 + \sum_j \langle \beta_j | \phi_n \rangle \quad (3.27)$$

where β_i represents the projector functions that depend on the ionic positions, and the augmentation function $Q_{ij}(r)$ given as:

$$Q_{ij}(r) = \psi_i^*(r)\psi_j(r) - \phi_i^*(r)\phi_j(r) \quad (3.28)$$

where $\psi_i(r)$ are the all-electron wave-functions. The norm-conservation condition ($Q_{ij}(r) = 0$) is not satisfied in the construction of the ultra-soft wave functions, $\phi_i(r)$. And the orthonormal condition takes on a generalized form as:

$$\langle \phi_i | S(\{R_I\}) | \phi_j \rangle = \varepsilon_{ij} \quad (3.29)$$

where $S(R_I)$ depends on the ionic positions through $|\beta_i\rangle$ and is expressed as:

$$S = 1 + \sum_{ij} q_{ij} |\beta_j\rangle \langle \beta_i| \quad (3.30)$$

$$\text{where } q_{ij} = \int Q_{ij}(r)dr \quad (3.31)$$

3.5 Non-linear core correction in pseudopotential approximations

Pseudopotential approximations typically rely on the assumption that core and valence charge densities are sufficiently distinct, allowing the kinetic and exchange-correlation interactions to be treated as linear. However, when these densities significantly overlap, this simplification can introduce systematic errors in the total energy. This issue becomes more pronounced in spin-polarized calculations, which involve additional non-linear effects and require explicit treatment of the energy's non-linear dependence on the core charge density. Moreover, in magnetic systems particularly those involving transition metals, spin polarization arises from valence orbitals whose charge and spin densities intersect with those of the core electrons [201]. Therefore, it is crucial to accurately characterize the behaviour of wavefunctions near the core region to properly account for the influence of the surrounding environment on the exchange-correlation potential experienced by the valence electrons.

In the framework of the pseudopotential approximation, the overall exchange-correlation potential depends on the valence and core charge densities, as well as the spin polarization [202]. This relationship can be expressed implicitly as follows:

$$V_{xc}(\rho^v + \rho^c, p) = \underbrace{\left[V_{xc}(\rho^v + \rho^c, p) - V_{xc}(\rho^v, \rho^v) \right]}_{\text{included in the pseudopotential}} + \underbrace{V_{xc}(\rho^v, \rho^v)}_{\text{calculated}} \quad (3.32)$$

$$\text{where } \rho(r) = \frac{\rho_\alpha^v - \rho_\beta^c}{\rho^v(r) + \rho^c(r)} \quad (3.33)$$

denotes the spin polarization, while ρ^v and ρ^c represent the valence and core charge densities, respectively. Because the exchange-correlation potential depends on spin polarization, it becomes a nonlinear function of the total charge density. As a result, in spin-polarized systems, the ionic pseudopotential is influenced by the specific valence electron configuration. Consequently, incorporating nonlinear core corrections into the exchange-correlation potential is crucial for

accurately capturing the magnetic ordering behaviour of spin-polarized materials [201,203,204], including those examined in this study.

3.6 Numerical implementation of the Kohn-Sham equations

To solve the Kohn-Sham single particle equation, the electron wave function ψ_i for the orbitals must be known. However, the wave function depends on the electron density first, which is initially unknown. Thus, the Kohn-Sham equations are solved iteratively within a self-consistent field (SCF) approach. Initially, a starting charge density $\rho_1(r)$ is “guessed” to generate the starting wave functions. These wavefunction are then used to build the Kohn-Sham Hamiltonian, from which an improved charge density $\rho_2(r)$ is obtained. This process is repeated, with each iteration providing progressively better approximations of the electron density $\rho_{3,\dots,N}(r)$, until self-consistency is achieved, as illustrated in Figure 3.3 [205]. Consequently, the final quantities of interest—such as total energies, forces, stresses, and eigenvalues are extracted from the output file of any ab-initio quantum mechanical DFT code. Within the DFT framework, electronic structure calculations can simulate various properties of materials, such as structural, electronic, optical, phonon and mechanical characteristics, based solely on the assembly of electrons and nuclei, requiring no experimental data.

In this thesis, the Cambridge Serial Total Energy Package (CASTEP) software code of the Material Studio suite (version 2020) of was used [206,207]. The CASTEP is a plane wave pseudo-potential DFT code capable of modelling interfaces, solids, and surfaces across a wide range of materials, including alloys, semiconductors, ceramics, metals. CASTEP is widely recognized for its effectiveness in addressing challenges in engineering, chemistry, materials science, and solid-state physics.

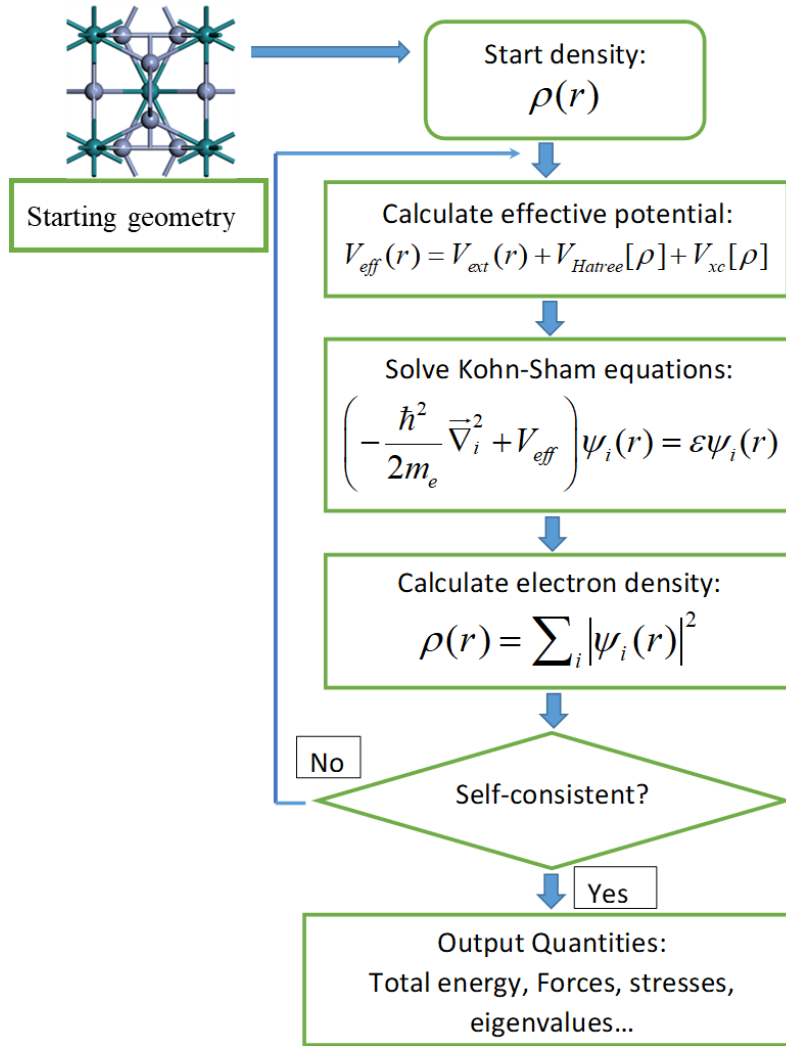


Figure 3.3: Schematic representation of the SCF method used in DFT

3.7 Other important aspects in solving the Kohn-Sham equations

To determine the ground state charge density, one must solve the Kohn-Sham equation (Equation 3.7 and 3.14), which involve an infinite set of single-electron equations. These equations incorporate the exchange-correlation potential typically treated within the Local (Spin) Density Approximation (L(S)DA) or the Generalized Gradient Approximation (GGA). A common strategy for constructing the Kohn-Sham single-particle orbitals ψ_m (Equations 3.8 and 3.15) is to represent the electronic wave function as a linear combination of basis functions, effectively expanding it within a chosen basis set.

$$\psi_m(r) = \sum_{P=1}^P c_P^m \phi_P^b(r) \quad (3.34)$$

The wave function ψ_m resides in an infinite-dimensional function space, and its solution hinges on identifying suitable expansion coefficients c_P^m that represent it in a chosen basis set ϕ_P^b [208]. Once a basis such as plane waves [180] is selected, and given the variational nature of the total energy, the expansion coefficients c_P^m become the sole variables in the problem. Solving the self-consistent Kohn-Sham equations thus involves finding the coefficients for the occupied orbitals that minimize the total energy. The standard approach entails optimizing and computing the self-consistent charge density. For a fixed charge density, the coefficients are iteratively refined using matrix-based methods to evaluate the system's total energy. This procedure effectively transforms the single-particle Kohn-Sham Schrödinger equation into a generalized eigenvalue problem.

$$\sum_{P=1}^P (H - \varepsilon_i S) c_P^m = 0 \quad (3.35)$$

Here, the energy-independent Hamiltonian and overlap matrices are denoted by H and S , respectively. The corresponding equation is solved at each point to perform integration over the irreducible wedge of the Brillouin zone (IBZ), which is sampled in three-dimensional k -space according to the local point symmetry of the structure under consideration. In practice, it is often not feasible to represent the exact occupied Kohn-Sham orbitals using a finite basis set. However, an approximate solution that minimizes the total energy can be obtained by employing a basis set of sufficiently high quality in conjunction with the self-consistent field (SCF) method, as detailed in Section 3.5. The adequacy of a basis set is typically assessed by comparing the total energy calculated from the basis set orbitals to the exact Kohn-Sham total energy. Moreover, an effective basis set should satisfy several criteria: it should be efficient, requiring a minimal number of functions to achieve a desired level of convergence; unbiased, meaning it does not preferentially weight certain spatial regions or favor specific solutions; mathematically simple, to facilitate the computation of matrix elements; and complete, in the sense that it can be systematically improved by adding more functions of the same type [180]. Kohn-Sham orbitals can be represented using

any appropriate complete basis set, with several options available. Among the most widely adopted are the Linear Combination of Atomic Orbitals (LCAO), Gaussian-type or Slater-type orbitals (GTOs or STOs), and plane wave basis sets [209].

Representing Kohn-Sham orbitals with plane wave basis sets offers several notable benefits over alternative basis choices [210]. These include the mathematical simplicity of plane waves, which impose no assumptions on the form of the solution, and the elimination of basis set superposition error. Plane waves also enable efficient force calculations on atoms. Moreover, Bloch's theorem naturally supports their use in periodic systems. A further computational advantage arises from the fact that the kinetic energy operator is diagonal in reciprocal space, while the potential energy operator is diagonal in real space allowing efficient transitions between these representations via Fast Fourier Transforms (FFT), thereby lowering computational cost [211]. Additionally, because plane wave basis sets are non-local, Pulay forces [206] do not emerge during force evaluations on ions, enhancing the accuracy and efficiency of such calculations.

A key limitation of the plane wave basis set is its computational inefficiency in full potential calculations [180], as accurately capturing atomic wavefunctions near the nucleus requires an impractically large number of basis functions. To address this challenge, pseudopotentials [212,213] or hybrid basis sets [180] are commonly employed to model atomic wavefunctions under steep potential variations. Consequently, the plane wave method for solving the Kohn-Sham equations is typically implemented in two ways: either as a full potential calculation or using pseudopotentials, depending on whether the plane waves account for the influence of all electrons in the atom or only the valence electrons, including semi-core states. The preceding section (3.4.2) provides a detailed explanation of both methods.

3.8 Geometry optimization

Geometry optimization is a vital tool in modelling material systems, aimed at refining initial geometries alongside physical properties such as lattice parameters and magnetic moments. This optimization seeks to identify the ground state energy corresponding to the system's most stable configuration. Accurate geometry optimization is essential as it influences the electronic properties

of the system and other properties that depend on the system's total energy. Initially, electronic properties are calculated based on a fixed initial geometry, from which forces acting on the atoms are derived. The position of the atoms is then iteratively updated through several self-consistent field (SCF) until it is reached, subject to a defined convergence tolerance limit.

In optimizing the geometry of a system, local minima are often obtained rather than the global minimum, with the resulting minimum being strongly influenced by the chosen initial geometry. Therefore, it is important to use as many relevant initial geometries as possible to provide maximum assurance of a global minimum being achieved [214,215]. Many geometry optimization techniques are based on the principle of finding the minimum of an energy hypersurface as a function of its atomic positions [214,215]. Other geometry approximation such as Quasi-Newtonian mechanics, optimize the total forces acting on a system [206,216], as discussed in the subsequent section.

3.8.1 Quasi-Newtonian geometry optimization

The Quasi-Newtonian geometry optimization algorithm uses the quadratic model of the multi-dimensional potential surface to obtain a global minimum. The geometry optimization equation for the potential energy hypersurface E' with optimization step s and the applied force f is given as:

$$E' = E - f^T s + \frac{1}{2} s^T P s \quad (3.36)$$

$$f' = f - P s \quad (3.37)$$

where P is the matrix of the second order derivative of the energy (Hessian matrix) or forces due to the respective geometries. At the minimum energy, the forces approach zero, and thus a global minimum is achieved (in equation 3.36) [206]. The algorithms applied in optimization are used to approximate the hessian matrix (or its inverse depending on the method used) such as the steepest descent, damped molecular dynamics or more sophisticated conjugate gradients or BFGS. The BFGS (Broyden-Fletcher-Goldfarb-Shanno) [217–220] is the most accurate approach applied in

Hessian update methods and has been used in all the calculations reported in this thesis, as implemented in the CASTEP [206] code.

In the BFGS approach, the next geometry iteration update for the Hessian matrix (P) minimization is given by:

$$P_{k+1} = P_k + \Delta P_k \quad (3.38)$$

for two consecutive iterations, ΔP_k is given by

$$\Delta P_k = \left[\frac{d_k d_k^T}{s_k^T d_k} + \frac{P_k s_k s_k^T P_k}{s_k s_k^T P_k} \right] \quad (3.39)$$

where, the gradient between two consecutive geometries is given by $d_k = f_k - f_{k+1}$ while the most common algorithm for optimization step size s is the trust-region or search line method [221]. The efficiency of the structure relaxation is critically dependent on both the initial geometry and the starting conditions of the hessian estimate. Typically, the initial estimate of the Hessian (P), is chosen as a unitary matrix. However, it can experience substantial variation during the minimization. In contrast to other geometry optimization approaches [222], the BFGS exhibits favorable behavior regarding Hessian estimate. Specifically, the BFGS update tends to converge to a stable estimate within a limited number of iterations. This behavior can be attributed to several factors, including the implementation of a skip strategy $P_{k+1} = P_k$ that allows calculations to proceed from the current geometric configuration, the use of an appropriately slanted initial Hessian estimate, and the incorporation of a damped BFGS update [221,222] to refine the Hessian estimate further. These characteristics contribute to the robustness of the BFGS method, facilitating efficient convergence toward the local minimum of the energy landscape. Consequently, careful consideration of the Hessian initialization and updating strategy is paramount for optimizing the overall relaxation process in computational materials science.

3.9 Brillouin zone sampling

A commonly used computational approach involves averaging periodic functions of the wave vector over the Brillouin zone [223]. These calculations are inherently complex and computationally demanding. In principle, they require knowledge of the function's value at every point within the Brillouin zone. However, electronic states are only allowed at discrete points determined by the boundary conditions of the bulk solid. According to Bloch's theorem, an infinite number of k-points corresponds to an infinite number of electrons in the system, since only a finite number of electronic states are occupied at each k-point. The total electric potential of the material can thus be evaluated by summing contributions from the occupied states at each k-point, which collectively determines the overall electronic current.

Because the potential and other relevant functions are generally smooth, an integral over an infinite number of k-points can be approximated by a summation over a finite and often small set of k-points. In density functional theory (DFT), this is achieved by sampling a limited number of k-points to represent the elements of k-space. To minimize computational effort while maintaining accuracy, specialized k-point schemes have been developed that use the fewest points necessary for a given precision. The most widely adopted is the Monkhorst-Pack method [224], while alternative sampling techniques have been proposed by Joannopoulos and Cohen [225], and Chadi and Cohen [226]. According to Monkhorst-Pack approach, the k-points are uniformly distributed throughout the Brillouin zone as follows:

$$k = x_1 y_1 + x_2 y_2 + x_3 y_3 \quad (3.40)$$

where y_1, y_2 and y_3 are variables of the inverse lattice of

$$x_i = \frac{1}{n_i} \quad (3.41)$$

where $l=1, \dots, n_l$, here n_i are the folding parameters indicate how the sampled k-points are arranged in rows or columns aligned with the zone-crossing reciprocal lattice vectors, and how

they are evenly distributed across the Brillouin zone. The required number of k-points for computation depends on the type of material being studied, such as metals, semiconductors, and insulators each demand different treatment. Metallic systems typically require significantly more k-points, often an order of magnitude higher than semiconductors or insulators, due to the need for dense k-space meshes to accurately resolve the Fermi surface. If the sampled k-points fail to yield a well-converged total energy, a much finer mesh must be employed to reduce errors and achieve reliable convergence. Thus, the key objective of convergence testing is to identify a sufficiently dense summation grid to ensure the accuracy of the computational results.

3.10 Computational code

Computational simulations of materials have emerged as a powerful and widely used approach in physics, chemistry, and materials science. These simulations help interpret experimental data, predict material properties, and guide the development of novel materials within the field.

3.10.1 Material studio

BIOVIA Materials Studio [227] is a comprehensive modeling and simulation platform tailored for computational researchers in materials science, physics, and chemistry. It enables prediction and analysis of how atomic and molecular structures relate to material properties and behavior. The software suite supports a wide range of applications, including studies on catalysts, composites, metals, and alloys. Material studio has an analytical and crystallization tool to facilitate the investigation, prediction, and modification of crystal structures and growth processes. Additionally, it allows for simulations of particle morphology, exploration of polymorphism, surface interaction studies, and the design of additives that influence growth. Materials Studio also provides capabilities for calculating various properties such as electronic, structural, thermodynamic, mechanical, phonon etc. All density functional theory (DFT) computations in this study were performed using the CASTEP module integrated within BIOVIA Materials Studio (Version 2020).

3.10.1. 1 The CASTEP Code

CASTEP [207] is a comprehensive first-principles quantum mechanical software designed for electronic structure calculations, offering a wide array of capabilities. Initially developed by Payne and collaborators in the late 1980s and early 1990s [228], it rapidly gained popularity as a reliable computational tool in this field. Within the framework of density functional theory (DFT), CASTEP can simulate various types of materials, including crystalline solids, surfaces, molecules, liquids, and amorphous systems. The central quantity in these simulations is the total energy, from which numerous other physical properties can be derived. Any material composed of nuclei and electrons can be modeled, constrained only by the computational limits of processing speed and memory. This method is notably ambitious, as it avoids empirical input and relies solely on quantum mechanical principles. Forces are obtained by differentiating the total energy with respect to atomic positions, while stresses arise from derivatives with respect to cell parameters. These outputs enable full geometry optimization and, when needed, finite-temperature molecular dynamics simulations of material systems.

3.11. Accuracy and reliability of DFT calculations

The Density functional theory has achieved notable progress across various scientific domains including high-temperature structural application, catalytic processes, electron transport, solar energy conversion, and drug design for medicinal applications [229,230]. The effectiveness of DFT is fundamentally reliant on the accuracy of the exchange-correlation functional; If this functional were precisely known, one could accurately describe the quantum mechanics of any system. However, because the exchange-correlation functional must be approximated to calculate the ground-state total energy of systems, the applicability of DFT is inherently limited.

DFT demonstrates commendable accuracy in predicting bond lengths of molecular systems, typically within 2% compared to experimental data, while vibrational frequencies are often overestimated by less than 5%. Nevertheless, the local density approximation (LDA), tends to over bind molecules by approximately 1 eV per bond, while the generalized gradient approximation (GGA), over binds on the order of 0.3 eV per bond. Hybrid functionals, further reduces this over

binding error by about 50%. Under this approach, DFT can estimate ionization energies and electron affinity to within approximately 0.2 eV of experimental observations [231].

Other than the inherent limitations arising from the choice of the exchange-correlation functional, computational errors can also arise from numerical computations, including the choice of the plane wave energy cut-off, and k-point sampling and size of the supercell, often due to computational resources constraints [232,233]. In this study, numerical computation errors arising from these variables have been minimized by enhancing their level of convergence. To ensure the accuracy of the results, a convergence criterion for energy, force displacement, and stress were set at 5.0×10^{-6} eV per atom, 0.01 eV/Å, and 0.02 GPa, while a temperature smearing width of 0.001 eV was set to ensure accuracy of the calculated magnetic moments [234–236]. This level of accuracy is essential in magnetic systems, where different magnetic states are often separated by energies on the order of meV, necessitating sufficiently converged quantum mechanical total energies to reliably discern these small energy differences. Despite these drawbacks, DFT is fundamentally robust and proficient in predicting a wide range of electronic and structural properties of material systems with good accuracy, compared to experimental data. The accuracy of DFT predictions depends on the specific property and other interrelated properties of the material being studied. Typically, quantitative discrepancies between DFT and experimental results typically exhibit consistent trends across different material systems. Thus, systematic errors for a particular DFT technique can often be corrected through experience and comparison with experimental data. For instance, when evaluating the formation energies of defects, comparing similar configurations while maintaining a constant number of atoms and charge state can result in the approximate cancellation of systematic errors and DFT approximations [237–239].

Chapter Four

Structural, electronic and mechanical stability of X_3Ru in A15, D0c and tP16 in crystallographic phases

The Density functional theory (DFT) formulation described in Chapter 3 was applied to investigate the properties of X_3Ru alloys (where $X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu$ and Zn). These alloys were analyzed across various crystallographic phases, specifically A15, D0c and tP16, using the Cambridge Serial Total Energy Package (CASTEP) code. This chapter presents the thermodynamic, electronic and mechanical stability of each of these alloy systems at zero pressure, as well as the computational parameters utilized in the calculations.

Key aspects of the study include the evaluation of the alloy heats of formation, electronic band structures, and elastic moduli, which provide insights into the thermodynamic and mechanical stability the X_3Ru alloys in A15, D0c and tP16 phases. By quantifying the heats of formation, the study establishes whether each X_3Ru alloy is thermodynamically stable under equilibrium conditions. This directly informs the feasibility of synthesizing these materials and highlights which systems are most promising for practical deployment. Identifying alloys with favorable formation energies helps narrow down potential candidates that can overcome the limitations of conventional nickel-based superalloys, which are already operating near their thermal limits.

Band structure and density of states analysis provides insight into the metallic nature and electron transport characteristics of the alloys. Efficient electron mobility is critical for maintaining conductivity and stability under extreme operating conditions. This aspect not only ensures structural integrity at elevated temperatures but also opens new avenues for multifunctional applications in electronics, energy systems, and magnetic devices.

The elastic constants and moduli reveal the alloys' resistance to deformation, compression, and structural collapse. These mechanical indicators are essential for determining whether the materials can withstand the stress encountered during the operation of turbine engines and other high-temperature mechanical systems. High bulk moduli and ductility point to alloys capability of

maintaining strength while reducing weight, thereby improving efficiency and performance in aerospace applications. Together, these three aspects - heats of formation, electronic band structures, and elastic moduli- provide a holistic framework for solving the main problem of the study: the urgent need for materials that surpass the performance limits of nickel-based superalloys. By integrating thermodynamic, electronic, and mechanical evaluations, they not only identify stable candidates such as A15 Cr_3Ru but also uncovers valuable properties in alloys predicted to be unstable. This dual perspective expands the design space, offering new insights into how Ru-based systems can be tailored for multifunctional roles.

The novelty of the current study also lies in demonstrating that even alloys with inherent thermodynamic challenges can exhibit desirable mechanical and electronic properties, thereby positioning them as potential candidates for targeted engineering solutions. This comprehensive approach advances the understanding of Ru-based alloys and contributes to the broader effort of developing materials that combine high-temperature resilience, lightweight character, and multifunctionality for aerospace and energy applications.

4.1 Computational parameters

Ab-initio DFT calculations [240,241] were performed to investigate the structural, electronic and mechanical properties of 3d-transition X_3Ru alloys in cubic A15, tetragonal D0c and tP16 crystallographic phases. These calculations were performed using the CASTEP code [206], with each alloy modelled from their respective unit cell, as illustrated in Figure 4.1. The interaction between the core and valence electrons was described by the Vanderbilt ultrasoft pseudopotential [199], with a converged plane wave cut-off of 800 eV, while the electronic exchange correlation was described by the Perdew–Burke–Ernzerhof Generalized Gradient Approximation (PBE-GGA) functional incorporating the Hubbard parameter ($U = 2.5$ eV) [242,243]. The value of U in this study was chosen to accurately reproduce the experimental lattice parameters and magnetic moments of the constituent elements X ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) [234–236].

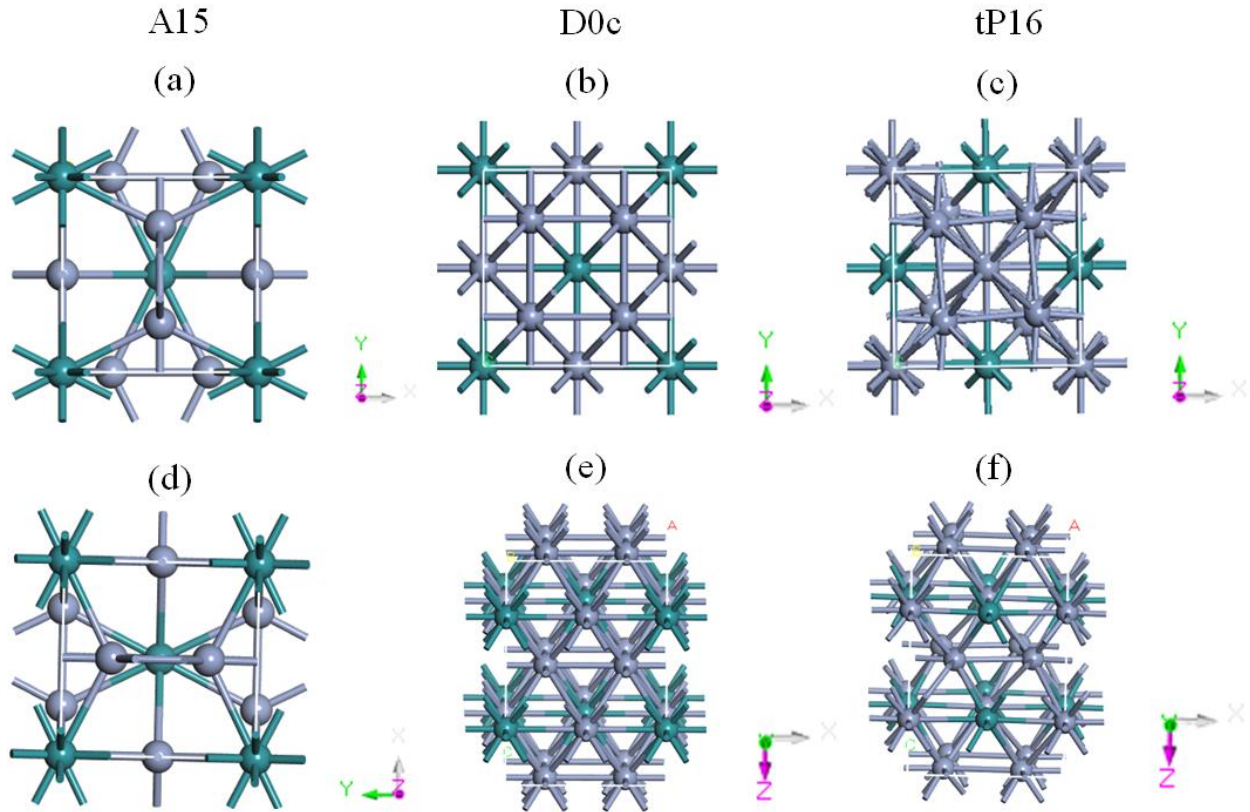


Figure 4.1: Crystal structures of (a) cubic A15, (b) D0c, and (c) tP16 phases of Ru–Cr alloys, with corresponding top views shown in (d), (e), and (f). Green spheres represent Ru atoms, while gray spheres represent Cr atoms.

To validate the reliability of our computational parameters, Table 4.1 presents a comparison of the calculated magnetic moments and lattice parameters with experimental parameters for single 3d-transition metals. The results indicate that our calculated lattice parameters are in good agreement with the experimental values, thereby confirming the robustness of computational models. For each system, the single point energy and geometry optimizations were conducted using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) technique. To ensure accuracy and reliability of the calculated results, the self-consistent field (SCF) convergence criteria on energy, force, atomic displacement, and stress were set at 5.0×10^{-6} eV per atom, $0.01 \text{ eV } \text{\AA}^{-1}$, $0.0005 \text{ \AA}$, and 0.02 GPa , respectively. Similarly, to ensure an accurate representation of the magnetic properties of these systems, the smearing width was set at 0.001 eV . These convergence values have been found to yield reliable results, across a wide range of material systems [206].

Table 4.1: Calculated lattice parameters and magnetic moments of the studied pure 3d-transition metal (X) and ruthenium-add values compared to experimental data where available

Transition metal	lattice parameters (Å)	Magnetic moments (μ_B/atom)
Sc	3.41	0.95
	3.31 [244]	
Ti	2.99	2.09
	2.95 [244]	
V	3.03	0.79
	3.03 [244]	
Cr	2.85	0.00
	2.88 [245]	
Mn	8.91	5.00
	8.91 [244]	4.50 [246]
Fe	2.88	2.64
	2.87 [244]	2.20 [247]
Co	2.51	1.68
	2.51 [244]	1.70 [247]
Ni	3.53	1.28
	3.52 [244]	0.60 [247]
Cu	3.64	0.00
	3.61 [244]	
Zn	2.63	0.00
Ru	2.71	0.00
	2.71 [244]	

In addition to the SCF convergence criteria, the accuracy of DFT results depends on the size of the plane-wave cutoff energy and the number of k-points sampled. Figure 4.2 illustrates the plane-wave cutoff energy convergence showing a converged value of 800 eV, while Figure 4.3 presents the Monkhorst-Pack [248] k-points convergence results with converged values of $15 \times 15 \times 15$, $15 \times 15 \times 10$ and $15 \times 15 \times 11$ for the A15, D0c and tP16 phases, respectively. The corresponding accuracy from these converged plane-wave cutoff energy and k-points is 0.01 eV and 0.001 eV, respectively, confirming the robustness of the computational parameters used in this study.

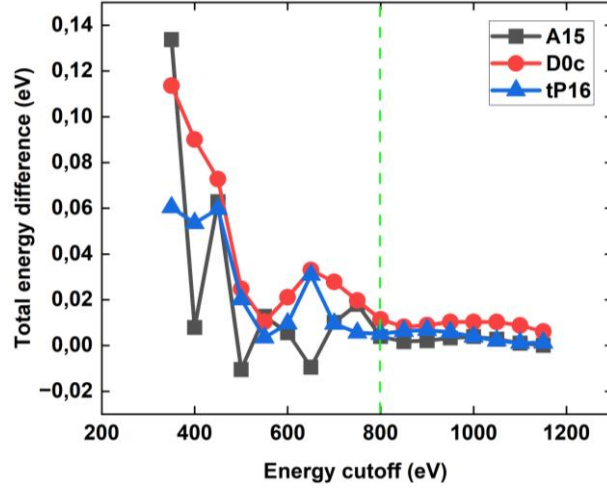


Figure 4.2: The total energy difference versus the plane wave energy cutoff for A15, D0c and tP16 Cr₃Ru alloys.

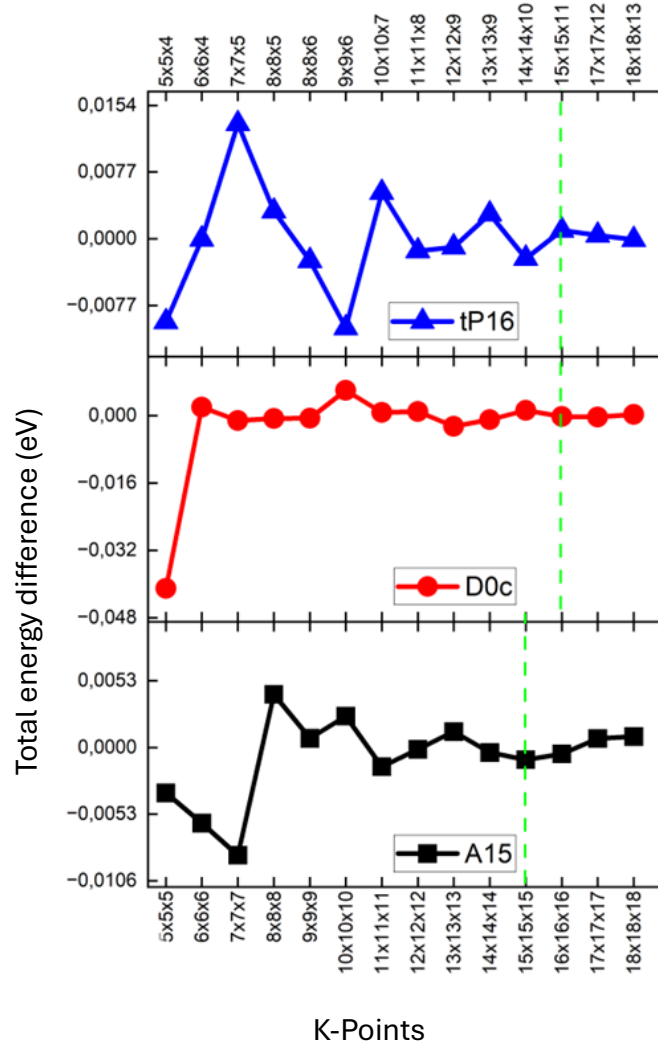


Figure 4.3: Total energy difference versus the K-points for A15, D0c and tP16 Cr₃Ru alloys.

4.2 Thermodynamic stability

The stability of a material is a critical factor in its application and performance, primarily describing its resistance to chemical change physical degradation. On the other hand, the structural properties of a material are fundamentally characterized by the atomic interaction within the unit cell. In this study, the stability of A15, D0c, tP16 X₃Ru-based alloys is characterized in terms of their heat of formation. First-principles studies have demonstrated that the heat of formation can reliably predict alloy stability, hence, examining the heat of formation of alloys in their different compositions is an effective approach for assessing thermodynamic stability of alloys.

For a given material system, the heat of formation ΔH_f is defined as the amount of energy needed to form or break chemical bonds, and is calculated as:

$$\Delta H_f = \left[\frac{E(A_x B_y) - [xE(A) + yE(B)]}{x + y} \right] \quad (4.1)$$

where, $E(A_x B_y)$, $E(A)$ and $E(B)$ are the equilibrium total energies of the alloy system AB and that of the individual elemental species A and B , with atomic concentrations x and y . Negative heat of formation indicates a thermodynamically stable system, while a positive value indicates an unstable or metastable system, at equilibrium conditions.

Figure 4.1 illustrates the crystal structures of Ruthenium-based transition metal alloys, X₃Ru (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) in A15, D0c and tP16 phases. The A15 phase consists of X atoms occupying six equivalent positions in c-site (0.25, 0, 0.5) and Ru atoms that occupy bcc positions (0, 0, 0). In contrast, the D0c phase exhibits a body-centered tetragonal structure with space group I4/mcm. Within this unit cell, Ru atoms are positioned at Wyckoff site 4a (0, 0, 0.25), whereas X atoms are located at 4b (0, 0.5, 0.25) and 8h (0.25, 0.75, 0). Meanwhile, the tP16 phase crystallizes in a tetragonal phase belonging to the space group P4/mbm. The Ru atoms occupy 4f (0, 0.5, 0.258) positions, while the X atoms are located at X1: 4e (0, 0, 0.251), X2: 4g (0.231,

0.731, 0), and X3 :4h (0.29, 0.29, 0.5) sites. Table 4.2, 4.3 and 4.4 present the calculated lattice parameters, heat of formation, magnetic moments, density and bond-length (X-Ru) of X₃Ru alloys in the A15, D0c and tP16 phases. The lattice parameters of these alloys vary systematically with the position of the transition-metal atoms within the 3d series. This indicates that the alloys are not arbitrary; rather, they display a consistent pattern that reflects the fundamental physical principles governing transition metals across the 3d series. Notably, alloys composed of transition metals positioned centrally (Fe) in the series exhibit lower lattice parameters compared to those containing early (Sc) or late (Zn) series elements (See Fig. 4.4) for all the studied phases. This result is consistent with the trends of atomic radii, bond length and electron densities of transition metal atoms across the 3d series. The observed trends in the lattice parameters effectively correlate with the bond-lengths, as evidenced by smaller X-Ru bond-lengths (See Fig. 4.4 (e)) being associated with reduced lattice parameters for D0c and tP16 phases.

It is important to note that the proposed X₃Ru alloys investigated in this study are relatively new; consequently, fundamental data available in the literature remains scarce. To validate the computational model, reference is made to the A15 Cr₃Ru phase, which is the only alloy from this series that has been experimentally synthesized to date. As shown in Table 4.2, the computed lattice parameters for A15 Cr₃Ru (5.59 Å) and A15 Ni₃Ru (4.84 Å) structures are consistent with values reported in other theoretical investigations Cr₃Ru (4.613 Å [249], 4.631 Å [162], and 4.623 Å [167]) and Ni₃Ru (4.57 Å) [249] confirming the accuracy of our results. The slight discrepancies between our calculated lattice parameters for Cr₃Ru (5.26 Å) and previously reported theoretical data (4.63 Å [162]), as shown in Table 4.2, can largely be attributed to differences in the exchange–correlation functionals employed. Whereas previous studies primarily utilized the GGA functional, our work employs GGA+U with U = 2.5 eV, which accounts for the observed variation. In addition, the calculated lattice parameters for D0c and tP16 Cr₃Ru (5.86 Å and 5.82 Å) compare reasonably with the reported value of 5.20 Å [162], as presented in Tables 4.3 and 4.4, respectively. Further validation of the computational models is demonstrated by the close agreement between the calculated lattice parameters of the constituent metals and the corresponding experimental data [244], as summarized in Table 4.1. In comparing the studied phases, the lattice parameters of D0c and tP16 are generally similar across all cases, except for Ti₃Ru, where D0c (5.82 Å) is larger than tP16 (5.40 Å). This can be attributed to atomic size effects and crystal structure dependence. The

Ti₃Ru anomaly demonstrates that distinctive electronic configurations and bonding arrangements can disrupt the general trend, indicating that lattice parameters are governed not only by atomic size but also by bonding physics specific to each phase. Overall, the A15 phase consistently exhibits the lowest lattice parameters among the studied 3d transition-metal alloys, relative to both D0c and tP16 phases. This behavior may be attributed to atomic packing efficiency, bonding characteristics, and systematic periodic influences. Despite variations in atomic radii across the 3d series, the structural features of the A15 phase consistently enforce smaller lattice parameters. This illustrates that crystal structure can supersede atomic size effects, producing a systematic trend across different alloys.

Table 4.2: Optimized equilibrium lattice parameter, heat of formation, magnetic moments, density and bond-length X-Ru (in Å) of A15-type X₃Ru alloys.

A15 Alloys	Lattice parameter (Å)	Heat of formation (eV/atom)	Magnetic moment (μ_B /atom)	Density (g/cm ³)	Bond-length (X-Ru) in Å
Sc ₃ Ru	5.51	1.09	0.01	4.48	3.08
Ti ₃ Ru	5.15	0.88	0.27	5.94	2.88
V ₃ Ru	5.15	0.79	0.03	6.16	2.88
Cr ₃ Ru	5.26	-0.49	0.22	4.88	3.13
	4.623[162] ^{theo}	0.08 [249]			
	4.61 [249] ^{theo}				
	4.62 [250] ^{theo}				
	4.637 [251] ^{exp}				
Mn ₃ Ru	5.37	-0.64	2.59	5.72	3.00
Fe ₃ Ru	4.90	1.34	1.58	7.57	2.74
Co ₃ Ru	4.90	1.41	1.70	7.85	2.74
Ni ₃ Ru	4.84	2.11	1.00	8.13	2.70
	4.57 [249]				
Cu ₃ Ru	4.97	1.12	0.40	7.89	2.78
Zn ₃ Ru	5.24	1.02	0.01	6.86	2.93

Table 4.3: Optimized equilibrium lattice parameters, heat of formation, magnetic moments, density and bond-length X-Ru (in Å) of D0c-type X₃Ru

D0c Structures	Lattice parameters (Å)	Heat of formation (eV/atom)	Magnetic moments (μ _B /atom)	Density (g/cm ³)	Bond-length (X- Ru) in Å
Sc ₃ Ru	6.24	-0.08	0.72	4.54	3.13
Ti ₃ Ru	5.82	-0.37	1.35	5.86	2.90
V ₃ Ru	5.74	-0.27	2.19	6.31	2.87
Cr ₃ Ru	5.86	-0.51	2.97	5.94	2.95
	5.20 [162]	0.24 [162]			
Mn ₃ Ru	5.75	-1.61	3.25	6.57	2.88
Fe ₃ Ru	5.04	0.11	2.52	8.43	2.74
Co ₃ Ru	5.20	0.10	1.82	9.31	2.60
Ni ₃ Ru	5.14	0.92	1.08	9.55	2.57
Cu ₃ Ru	5.21	0.31	0.00	9.67	2.61
Zn ₃ Ru	5.36	-0.22	0.00	9.08	2.68

Table 4.4: Optimized equilibrium lattice parameters, heat of formation, magnetic moments, density and bond-length X-Ru (in Å) of tP16-type X₃Ru

tP16 Structures	Lattice parameters (Å)	Heat of formation (eV/atom)	Magnetic moment (μ _B /atom)	Density (g/cm ³)	Bond-length (X- Ru) in Å
Sc ₃ Ru	6.23	-0.18	0.02	4.50	3.11
Ti ₃ Ru	5.40	-0.41	0.89	6.01	2.70
V ₃ Ru	5.73	-0.27	2.19	6.34	2.73
Cr ₃ Ru	5.82	-0.53	3.03	6.73	3.02
	5.20 [162]	0.24 [162]			
Mn ₃ Ru	5.75	-1.61	3.25	6.56	2.88
Fe ₃ Ru	5.07	0.07		8.65	2.54
Co ₃ Ru	5.20	0.10	1.82	9.31	2.60
Ni ₃ Ru	5.15	0.92	1.08	9.55	2.57
Cu ₃ Ru	5.21	0.31	0.00	9.67	2.68
Zn ₃ Ru	5.36	-0.23	0.00	9.08	2.68

Table 4.5: The atomic radii, atomic radii difference, magnetic moments, electronic configuration and number of paired electrons of 3d transition metals from Sc-Zn bonded with central Ru atom [235].

Element	Atomic radii (pm)	Relative Ru-X atomic radii (pm)	Mag.mom /atom	Relative Ru-X magnetic moment (Ru=0.00 μ_B /atom)	Electronic configuration	No: of unpaired spin
Sc	162	16	0.95	0.95	[Ar] 3d ¹ 4s ²	2
Ti	147	31	2.09	2.09	[Ar] 3d ² 4s ²	1
V	134	44	0.79	0.79	[Ar] 3d ³ 4s ²	0
Cr	128	50	4.93	4.93	[Ar] 3d ⁵ 4s ¹	2
Mn	161	17	5.00	5.00	[Ar] 3d ⁵ 4s ²	2
Fe	156	22	2.64	2.64	[Ar] 3d ⁶ 4s ²	3
Co	152	26	1.68	1.68	[Ar] 3d ⁷ 4s ²	4
Ni	159	29	1.28	1.28	[Ar] 3d ⁸ 4s ²	5
Cu	145	33	0.00	0.00	[Ar] 3d ¹⁰ 4s ¹	3
Zn	142	36	0.00	0.00	[Ar] 3d ¹⁰ 4s ²	3

In Table 4.2, we note that the range of heats of formation for the A15 phase extends from -0.64 eV/atom (Mn_3Ru) up to 2.11 eV/atom (Ni_3Ru), with most of the positive values clustering near 1 eV/atom. The heats of formation for A15 Mn_3Ru (-0.64 eV/atom) and Cr_3Ru (-0.49 eV/atom) are negative, indicating thermodynamic stability. In contrast, Tables 4.3 and 4.4 show that the range of heats of formation for the D0c and tP16 phases extends from -1.61 eV/atom (Mn_3Ru), up to 0.92 eV/atom (Ni_3Ru). It is observed that Mn_3Ru (-1.61 eV/atom), Cr_3Ru (-0.51 eV/atom and -0.53 eV/atom), Ti_3Ru (-0.37 eV/atom and -0.41 eV/atom), V_3Ru (-0.27 eV/atom in both phases), Zn_3Ru (-0.22 eV/atom and -0.23 eV/atom), and Sc_3Ru (-0.08 eV/atom and -0.18 eV/atom) in D0c, and tP16 phases exhibit negative heats of formation, indicating thermodynamic stability with Mn_3Ru , being the most stable in both phases. Among all studied alloys, Mn_3Ru consistently possesses the most stable compound across the three phases, suggesting that these alloys can be synthesized under equilibrium experimental conditions. For all positive A15 alloys, the heats of formation exceed 0.79 eV/atom, with Ni_3Ru being the most unstable at 2.11 eV/atom. In the D0c phase, positive values range from 0.10 eV/atom (Co_3Ru) to 0.92 eV/atom (Ni_3Ru), while in the tP16 phase, they extend from 0.07 eV/atom (Fe_3Ru) to 0.31 eV/atom (Ni_3Ru), with Ni_3Ru consistently emerging as the most thermodynamically unfavorable alloy. In general,

alloys with positive heats of formation are unstable under equilibrium conditions, though they may still be realized using non-equilibrium techniques such as ion implantation, rapid quenching or thin film deposition [252]. These methods can trap atoms in metastable states by relying on kinetic control rather than thermodynamic favorability, thereby enabling the formation of alloys that would otherwise be unattainable.

Previous studies [250,253] have further demonstrated that doping these alloys with 3d transition metals can lower their heats of formation, thereby enhancing stability. Considering relative stability between the three phases, both D0c and tP16 X_3Ru alloys exhibit comparable heats of formation (Fig. 4.1(b)), while the A15 phase consistently shows significantly higher formation energies. This higher energy is attributed to the relatively larger X–Ru bond length in the A15 phase compared to D0c and tP16 (Fig. X(e)). Notably, the heats of formation for A15 Cr_3Ru (–0.49 eV/atom), D0c Cr_3Ru (–0.51 eV/atom), and tP16 Cr_3Ru (–0.53 eV/atom) are closely comparable, with the tP16 Cr_3Ru alloy being the most stable. In general, the heats of formation for A15 alloys are higher compared to D0c and tP16, with only Mn_3Ru and Cr_3Ru remaining stable in an inverse relationship compared to the lattice parameters across all phases. The A15 phase requires greater energy for formation compared to D0c and tP16, indicating less favorable bonding interactions and reduced stability in most alloys. Only Mn_3Ru and Cr_3Ru exhibit negative heats of formation, confirming their true thermodynamic stability. This trend demonstrates that structure and stability are not always directly correlated. It also underscores the subtle interplay between geometry (lattice parameters) and energetics (heats of formation), emphasizing that both atomic physics and crystal chemistry must be considered.

Importantly, a significant correlation is observed between the calculated heats of formation and the relative atomic radii of the 3d elements in comparison to ruthenium. Smaller relative atomic radii correspond to lower heats of formation, while larger radii lead to higher values, a trend explained by crystal strain effects. This indicates that stability is governed by predictable physical laws rather than being arbitrary. Consequently, atomic size mismatches generate crystal strain, which in turn determines thermodynamic favorability. Furthermore, a strong direct correlation exists between the heats of formation of the X_3Ru alloys and their magnetic moments. Alloys with higher magnetic moments exhibit greater stability, as shown in Fig. 4.4(b, c).

Bond length (or bond distance) refers to the average separation between the nuclei of two atoms that are chemically bonded within a molecule. This is an indicator for bond strength, bond order, and atomic interactions. It can be determined through experimental techniques such as X-ray diffraction, as well as computational approaches like the CASTEP code in Materials Studio. In this section, the bond lengths have been calculated using the CASTEP code. In Table 4.2, the bond lengths for the A15 phase range from 2.704 Å (Ni₃Ru) to 3.126 Å (Cr₃Ru), with Cr₃Ru showing the largest value. This indicates a more relaxed lattice with reduced strain and enhanced bond stability. Other compounds with relatively long bond lengths include Sc₃Ru (3.081 Å), Mn₃Ru (2.999 Å), Zn₃Ru (2.929 Å), V₃Ru (2.881 Å), and Ti₃Ru (2.880 Å), all suggesting greater bond stability. By contrast, Cu₃Ru (2.779 Å), Fe₃Ru (2.741 Å), Co₃Ru (2.738 Å), and Ni₃Ru (2.704 Å) exhibit shorter bond lengths, reflecting weaker bonding. The order of increasing bond length is: Cr₃Ru > Sc₃Ru > Mn₃Ru > Zn₃Ru > V₃Ru > Ti₃Ru > Cu₃Ru > Fe₃Ru > Co₃Ru > Ni₃Ru. Generally, longer atomic separations reduce orbital overlap, but in solid-state systems they can also minimize repulsion and promote more stable crystal arrangements. In comparison, Table 4.3 shows that the bond-lengths for the D0c phase extend from 2.574 Å (Ni₃Ru) to 3.126 Å (Sc₃Ru), with Sc₃Ru being the highest. Other compounds with relatively large bond-lengths include Cr₃Ru (2.945 Å), Ti₃Ru (2.901 Å), Mn₃Ru (2.876 Å), and V₃Ru (2.869 Å). These values similarly indicate stronger, more stable bonds. Conversely, compounds such as Fe₃Ru (2.737 Å), Zn₃Ru (2.678 Å), Cu₃Ru (2.607 Å), Co₃Ru (2.597 Å), and Ni₃Ru (2.574 Å) exhibit shorter bond-lengths, suggesting weaker bonding. The order of increasing bond-length is Sc₃Ru > Cr₃Ru > Ti₃Ru > Mn₃Ru > V₃Ru > Fe₃Ru > Zn₃Ru > Cu₃Ru > Co₃Ru > Ni₃Ru. This suggests that longer bond lengths typically correspond to reduced lattice strain and enhanced bond stability. Table 4.4 shows that the bond lengths in the tP16 phase range from 2.535 Å (Fe₃Ru) to 3.114 Å (Sc₃Ru), with Sc₃Ru exhibiting the largest value. Other compounds with relatively high bond lengths include Cr₃Ru (3.022 Å), Mn₃Ru (2.874 Å), V₃Ru (2.730 Å), and Ti₃Ru (2.699 Å). These longer bond lengths suggest stronger and more stable bonds. In contrast, compounds such as Zn₃Ru (2.679 Å), Cu₃Ru (2.607 Å), Co₃Ru (2.598 Å), Ni₃Ru (2.574 Å), and Fe₃Ru (2.535 Å) display shorter bond lengths, indicating weaker bond strength and stability. The order of increasing bond length is: Sc₃Ru > Cr₃Ru > Mn₃Ru > V₃Ru > Ti₃Ru > Zn₃Ru > Cu₃Ru > Co₃Ru > Ni₃Ru > Fe₃Ru. Longer bond lengths are generally associated with reduced lattice strain and improved bond stability.

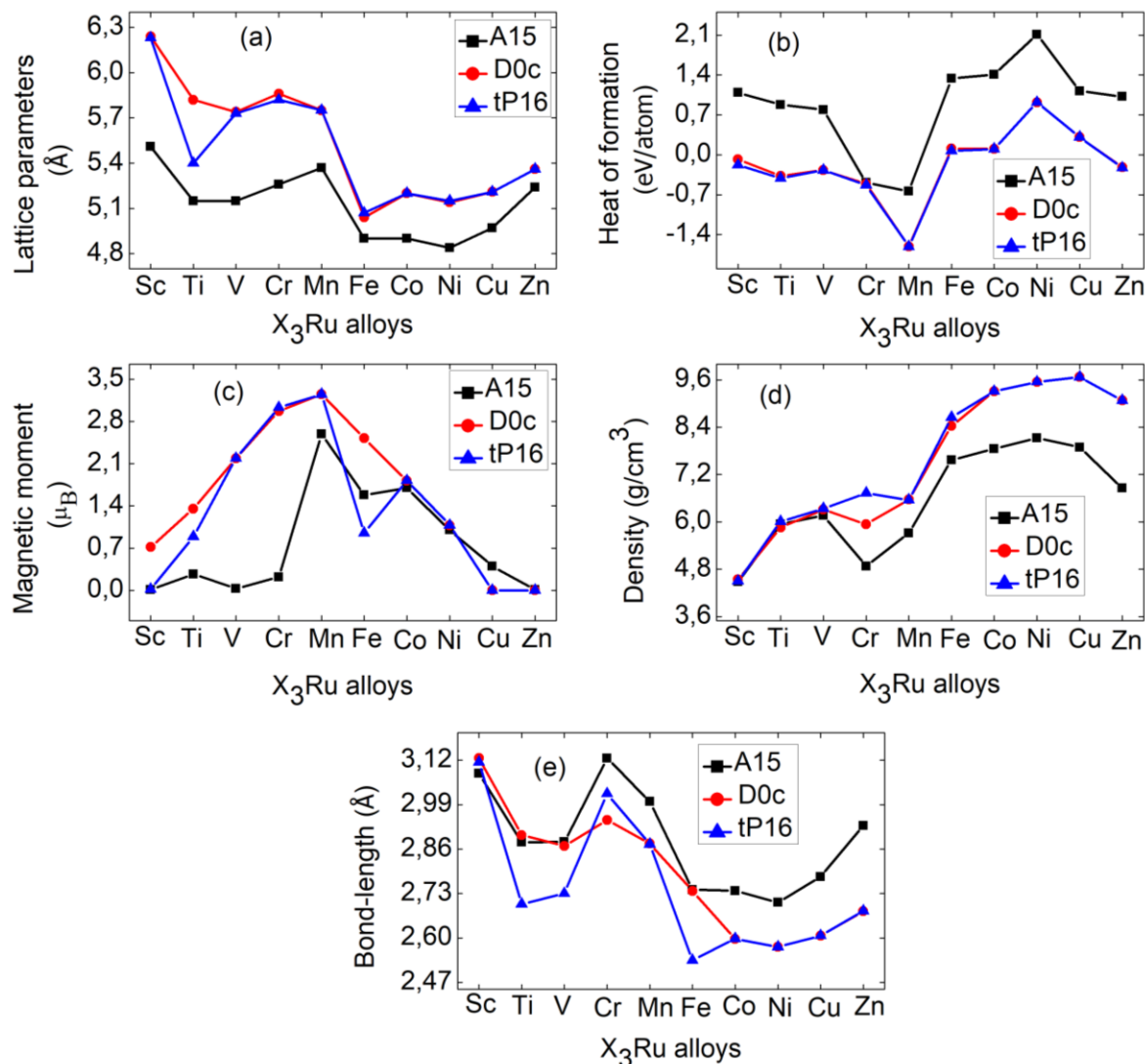


Figure 4.4: Calculated (a) lattice parameters (Å), (b) heat of formation (eV/atom), (c) magnetic moments (μ_B /atom), (d) density (g/cm^3) and (e) bond-length (Å) for A15, D0c and tP16 X_3Ru (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) compounds.

Across the D0c and tP16 phases, Sc_3Ru (thermodynamically stable) consistently exhibits the highest bond length, implying the strongest and most stable bonding. By contrast, in the A15 phase, Cr_3Ru possesses the largest bond length, reflecting the greatest bond stability in that structure. Furthermore, the bond lengths of Co_3Ru , Ni_3Ru , Cu_3Ru , and Zn_3Ru are longer in the A15 phase compared to their closely comparable values in the D0c and tP16 phases. This highlights the influence of crystal symmetry and coordination environment on bond distances. Overall, a clear correlation is observed between bond length and lattice parameters: for Sc_3Ru , Co_3Ru , Ni_3Ru ,

Cu₃Ru, and Zn₃Ru in the D0c and tP16 phases, the bond lengths are closely aligned (Fig. 4.4(e)), and this trend is consistently reflected in the lattice parameters (Fig. 4.4(a)). This is due to the unit cell dimensions being directly determined by the average bond distances.

Therefore, it is concluded that variations in bond length directly translate into variations in lattice parameters, demonstrating that atomic-scale electronic structure and bonding govern the overall dimensions and stability of the crystal in the A15, D0c, and tP16 phases.

4.3 Density

The use of material in lightweight applications, particularly in the aviation industry, is significantly influenced by its density. Density serves as key indicator of a material's weight and plays a crucial role, especially in the rotating components of aircraft wings and turbine blades. Within the DFT framework, density is calculated as

$$\rho^{cal} = \left[\frac{M_w * N}{Vol * A_0} \right] \quad (4.2)$$

where Vol is the volume of the unit cell, M_w is the average molecular weight of the elements in the unit cell, N is the total number of atoms and A_0 is the Avogadro's number (6.022×10^{23}). Tables 4.2, 4.3 and 4.4 provide the calculated densities for each of the X₃Ru alloys in the A15, D0c and tP16 phases, while Figure 4.4 (d) illustrates the density trends across the 3d transition series.

In Table 4.2, the densities of the A15 phase range from 4.48 g/cm³ (Sc₃Ru) to 8.13 g/cm³ (Ni₃Ru). The thermodynamically stable Mn₃Ru (5.72 g/cm³) and Cr₃Ru (4.88 g/cm³) alloys, as well as the unstable Sc₃Ru (4.48 g/cm³), all exhibit densities lower than that of the commonly used L1₂ Ni₃Al (6.14 g/cm³) [53], which is favored for lightweight high-temperature applications. Alloys with densities exceeding Ni₃Al, including V₃Ru (6.16 g/cm³), Fe₃Ru (7.57 g/cm³), Co₃Ru (7.85 g/cm³), and Ni₃Ru (8.13 g/cm³), are unsuitable for such applications due to their weight. The order of

decreasing density is: $\text{Ni}_3\text{Ru} > \text{Cu}_3\text{Ru} > \text{Co}_3\text{Ru} > \text{Fe}_3\text{Ru} > \text{Zn}_3\text{Ru} > \text{V}_3\text{Ru} > \text{Ti}_3\text{Ru} > \text{Mn}_3\text{Ru} > \text{Cr}_3\text{Ru} > \text{Sc}_3\text{Ru}$. Heavier transition metals such as Ni, Co, and Fe contribute greater atomic mass, while the compact packing of the A15 lattice reduces unit cell volume, resulting in higher densities. In contrast, lighter elements such as Sc, Cr, and Mn yield lower atomic mass and larger lattice spacing, producing reduced densities. As expected, X_3Ru alloys with smaller lattice parameters exhibit higher densities, with values increasing from Sc to Cu across the 3d series. This trend can be explained by the corresponding X–Ru bond lengths.

In Table 4.3, the densities of the D0c phase range from 4.54 g/cm³ (Sc_3Ru) to 9.67 g/cm³ (Ni_3Ru). The thermodynamically stable alloys Sc_3Ru (4.54 g/cm³), Ti_3Ru (5.84 g/cm³), and Cr_3Ru (4.88 g/cm³) all exhibit densities lower than $\text{L}_{12}\text{Ni}_3\text{Al}$ (6.14 g/cm³) [53], which is widely used in lightweight high-temperature applications. By contrast, alloys such as V_3Ru (6.31 g/cm³), Mn_3Ru (6.57 g/cm³), Fe_3Ru (8.43 g/cm³), Co_3Ru (9.13 g/cm³), Ni_3Ru (9.55 g/cm³), and Cu_3Ru (9.67 g/cm³) exceed the density of Ni_3Al and are unsuitable for lightweight applications due to their weight. The order of decreasing density is: $\text{Cu}_3\text{Ru} > \text{Ni}_3\text{Ru} > \text{Co}_3\text{Ru} > \text{Fe}_3\text{Ru} > \text{Mn}_3\text{Ru} > \text{V}_3\text{Ru} > \text{Ti}_3\text{Ru} > \text{Cr}_3\text{Ru} > \text{Sc}_3\text{Ru}$.

In Table 4.4, the tP16 phase shows densities ranging from 4.50 g/cm³ (Sc_3Ru) to 9.67 g/cm³ (Cu_3Ru). Stable alloys such as Sc_3Ru (4.50 g/cm³) and Ti_3Ru (6.01 g/cm³) are slightly less dense than Ni_3Al , making them promising candidates for lightweight high-temperature structural applications. Conversely, alloys including V_3Ru (6.34 g/cm³), Mn_3Ru (6.56 g/cm³), Fe_3Ru (8.65 g/cm³), Co_3Ru (9.31 g/cm³), Ni_3Ru (9.55 g/cm³), Cu_3Ru (9.67 g/cm³), Zn_3Ru (9.08 g/cm³), and Cr_3Ru (6.73 g/cm³) all exceed the density of Ni_3Al and are therefore unsuitable for such applications. The order of decreasing density is: $\text{Cu}_3\text{Ru} > \text{Ni}_3\text{Ru} > \text{Co}_3\text{Ru} > \text{Fe}_3\text{Ru} > \text{Zn}_3\text{Ru} > \text{Cr}_3\text{Ru} > \text{Mn}_3\text{Ru} > \text{V}_3\text{Ru} > \text{Ti}_3\text{Ru} > \text{Sc}_3\text{Ru}$.

The differences in density among these alloys in A15, D0c and tP16 phases stem directly from atomic mass and crystal packing, illustrating how microscopic electronic and structural characteristics scale up to determine their suitability for lightweight high-temperature structural applications.

Figure 4.4 (d) the densities for all the compounds in A15, D0c and tP16 phases indicate that Sc_3Ru , Ti_3Ru , V_3Ru , Cr_3Ru and Mn_3Ru possess the lowest densities compared to Fe_3Ru , Co_3Ru , Ni_3Ru , Cu_3Ru and Zn_3Ru alloys. The stable Sc_3Ru , Ti_3Ru in D0c and tP16 phases have the lowest densities whilst, the unstable Sc_3Ru , Ti_3Ru in A15 phase also indicates the lowest densities. Despite having the lowest density values, the stable Sc_3Ru and Ti_3Ru alloys demonstrate that stability is influenced not only by density but also by bonding interactions and electronic structure. In addition, these two structures in D0c and tP16 phases have the highest lattice parameters compared to other compounds, reinforcing the principle that larger atomic spacing lowers density.

4.4 Electronic and magnetic properties

The electronic properties of solids are fundamental to understanding their behavior and applications, as they define the allowed energy levels that electrons may occupy. One of the important concepts in the solid-state physics of metals is the Fermi level, which significantly influences the stability of materials. In metallic substances, the absence of a bandgap means the Fermi level lies within partially filled bands, allowing strong overlap of electronic states and resulting in metallic conductivity. In contrast, semiconductors and insulators exhibit a distinct bandgap, preventing overlaps between the valence and conduction bands.

In this Section, we focus on the electronic and magnetic properties of binary transition metal-Ru-based alloy X_3Ru through the analysis of the density of states. To ensure accurate and reliable density of states plots, in addition to the computational parameters outlined in Section 4.1, the accuracy of the interpolation integration method was set to fine accuracy level. This approach allows capturing detailed electronic characteristics that are vital for predicting material behavior and potential applications.

Magnetic moments serve as key parameters for determining whether a material is magnetic. A material with a magnetic moment below $0.3 \mu_B$ is classified as non-magnetic, whereas values above $0.3 \mu_B$ indicate magnetic behavior. Moreover, the magnitude of the magnetic moment can be explained and supported by the material's electronic properties, such as its density of states. In Table 4.2, the magnetic moments (μ_B) for the A15 phase range from $0.01 \mu_B$ (Sc_3Ru and Zn_3Ru)

to $2.59 \mu_B$ (Mn_3Ru), with Mn_3Ru exhibiting the largest value. Other compounds with relatively high magnetic moments (μ_B) include Fe_3Ru ($1.58 \mu_B$), Co_3Ru ($1.70 \mu_B$) and Ni_3Ru ($1.00 \mu_B$). These magnetic moments suggest that these compounds are magnetic. By contrast, compounds such as Ti_3Ru ($0.27 \mu_B$), V_3Ru ($0.03 \mu_B$), Cr_3Ru ($0.22 \mu_B$), Cu_3Ru ($0.40 \mu_B$) and Zn_3Ru ($0.01 \mu_B$) display low magnetic moments, indicative of non-magnetic behavior. The order of increasing magnetic moments is: $Zn_3Ru = Sc_3Ru < Cu_3Ru < Cr_3Ru < V_3Ru < Ti_3Ru < Ni_3Ru < Fe_3Ru < Co_3Ru < Mn_3Ru$. These observations indicate that the magnetic properties of these alloys reflect the fundamental principles of electron spin alignment in transition metals, with Mn_3Ru standing out as the most magnetic due to its electronic configuration and strong exchange interactions. Table 4.3 shows that the magnetic moments (μ_B) for the D0c phase extend from $0.00 \mu_B$ (Cu_3Ru and Zn_3Ru) to $3.25 \mu_B$ (Mn_3Ru), with Mn_3Ru exhibiting the highest value, reflecting maximum unpaired spin alignment and favorable orbital overlap with Ru. Other compounds with relatively large magnetic moments (μ_B) include Cr_3Ru ($2.97 \mu_B$), Fe_3Ru ($2.52 \mu_B$), V_3Ru ($2.19 \mu_B$), Co_3Ru ($1.82 \mu_B$), $1.35 \mu_B$ (Ti_3Ru) and $1.00 \mu_B$. These values similarly indicate magnetic character. This is because they possess strong magnetism due to partially filled d-orbitals that maximize spin polarization. Conversely, compounds such as Cu_3Ru ($0.00 \mu_B$), Zn_3Ru ($0.00 \mu_B$) and Sc_3Ru ($0.70 \mu_B$), exhibit smaller magnetic moments, suggesting non-magnetic signature. These alloys either possess fully filled d-orbitals (Cu, Zn) or nearly empty ones (Sc), leaving few or no unpaired electrons. Because exchange interactions are weak, the spins cancel out, resulting in non-magnetic behavior. The order of increasing magnetic moments is: $Cu_3Ru = Zn_3Ru < Sc_3Ru < Ti_3Ru < Ni_3Ru < Co_3Ru < V_3Ru < Fe_3Ru < Cr_3Ru < Mn_3Ru$. These observations indicate that the magnetic behavior of these alloys arises from fundamental electron configurations and spin physics. Mn_3Ru stands out as the most magnetic due to its high number of unpaired d-electrons and strong exchange interactions, whereas Cu_3Ru and Zn_3Ru remain non-magnetic because their d-orbitals are fully filled. Table 4.4 shows that the magnetic moments (μ_B) in the tP16 phase range from $0.00 \mu_B$, (Cu_3Ru and Zn_3Ru) to $3.25 \mu_B$ (Mn_3Ru), with Mn_3Ru exhibiting the largest value. Other compounds with relatively magnetic moments include Cr_3Ru ($3.03 \mu_B$), V_3Ru ($2.19 \mu_B$), Co_3Ru ($1.82 \mu_B$), Ni_3Ru ($1.08 \mu_B$) and $0.89 \mu_B$ (Ti_3Ru). These magnetic moments suggest magnetic behavior in these materials. In contrast, compounds such as Zn_3Ru ($0.00 \mu_B$), Cu_3Ru ($0.00 \mu_B$) and Sc_3Ru ($0.02 \mu_B$), display lowest magnetic moments, indicating weak to non-magnetic moments. The order of increasing magnetic moments is: $Zn_3Ru = Cu_3Ru < Sc_3Ru < Fe_3Ru < Ti_3Ru < Ni_3Ru < Co_3Ru < V_3Ru < Cr_3Ru < Mn_3Ru$.

Across all studied structures in the A15, D0c, and tP16 phases, Mn_3Ru exhibits the highest magnetic moment, identifying it as the most magnetic material, whereas Zn_3Ru shows the lowest value, indicating the least magnetic character. These observations indicate that the magnetic character of these alloys reflects fundamental electron configurations and spin physics. Mn_3Ru emerges as the strongest magnetic case due to its numerous unpaired d-electrons and robust exchange interactions, while Zn_3Ru remains the weakest because of its fully filled d-orbitals. As illustrated in Figure 4.4(c), the magnetic moments increase from Sc_3Ru , reach a maximum at Mn_3Ru , and then decrease toward Zn_3Ru . Furthermore, Mn_3Ru is also the most thermodynamically favorable, as evidenced by its lowest heat of formation across all phases (Fig. 4.4(b)). This indicates that the electronic configuration of Mn_3Ru supports both strong spin alignment, which gives rise to magnetism, and favorable bonding interactions, which enhance stability. This suggests that, within the studied phases, greater thermodynamic stability is associated with stronger magnetic behavior. This observation indicates that stable bonding environments enhance magnetic order, whereas unstable ones tend to weaken or suppress it. Magnetic compounds in the A15, D0c, and tP16 phases demonstrate potential for spintronic applications, particularly in spin-injection, as their electronic structures suggest they can sustain spin-polarized currents. Among them, Mn_3Ru is especially promising due to its combination of high stability and strong magnetism, although practical integration into devices such as USB drives and external hard drives remains an area of ongoing research.

4.4.1 Spin polarization and magnetization

Figure 4.5, 4.6 and 4.7 presents the spin-polarized total density of states (DOS) of X_3Ru ($\text{X} = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn) alloys across the A15, D0c and tP16 phases, respectively. The spin-polarized partial DOS showing the contribution from each constituent element is also presented in each of the figures. A significant behavior is the contrasting spin polarization across different alloy compositions and phases. For the D0c phase, we note that Zn_3Ru possesses symmetric spin up and spin down bands while in the tP16 phase, the symmetry of the spin-up and spin-down bands, is evident in Sc_3Ru , Cu_3Ru , and Zn_3Ru . This symmetric balance of the spin up and spin down bands leads to a cancelation of the magnetic moment associated with electronic

spin, thus explaining the zero calculated magnetic moments in these systems (Given in Table 4.4 and 4.5).

In contrast, the total density of states for the A15 phase in Ti_3Ru , V_3Ru , Cr_3Ru , Mn_3Ru , Fe_3Ru , Co_3Ru , Ni_3Ru and Cu_3Ru , Sc_3Ru and Zn_3Ru exhibits spin asymmetry. Similarly, the density of states for the D0c phase in Sc_3Ru , Ti_3Ru , V_3Ru , Cr_3Ru , Mn_3Ru , Fe_3Ru , Ni_3Ru , Co_3Ru as well as in the tP16 phase for V_3Ru , Cr_3Ru , Mn_3Ru , Fe_3Ru , Ni_3Ru , Ti_3Ru and Co_3Ru also shows asymmetric characteristics. These asymmetric density of states in the spin up and down bands account for the non-zero calculated magnetic moments reported in Tables 4.3, 4.4 and 4.5. As a result, these alloys demonstrate strong magnetic properties, making them promising candidates for spintronic applications, spin filters and spin injection technologies.

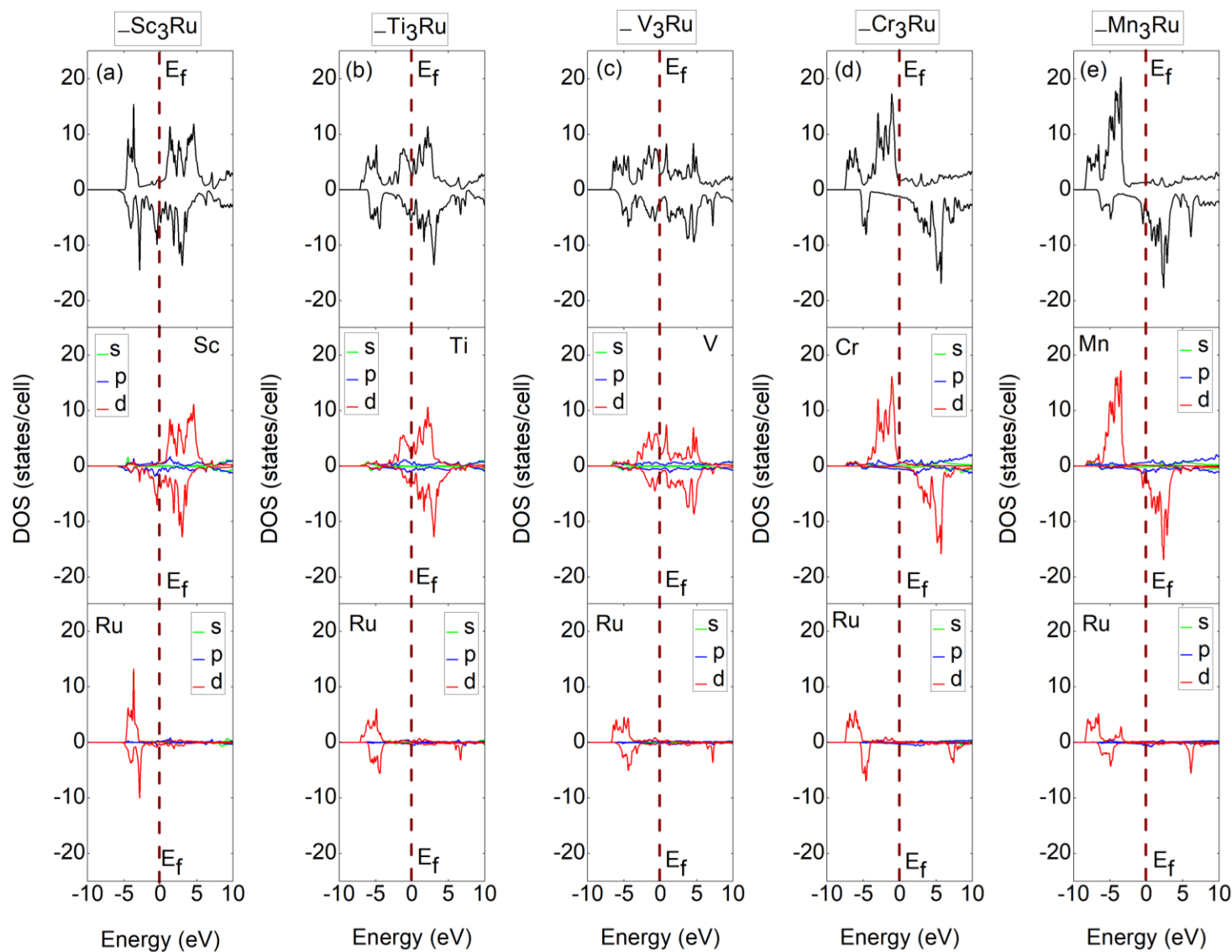


Figure 4.5 (a): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary A15 3d- X_3 Ru transition metal ($X = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}$ and Mn) calculated from GGA functional. Fermi energy is set to zero in each compound.

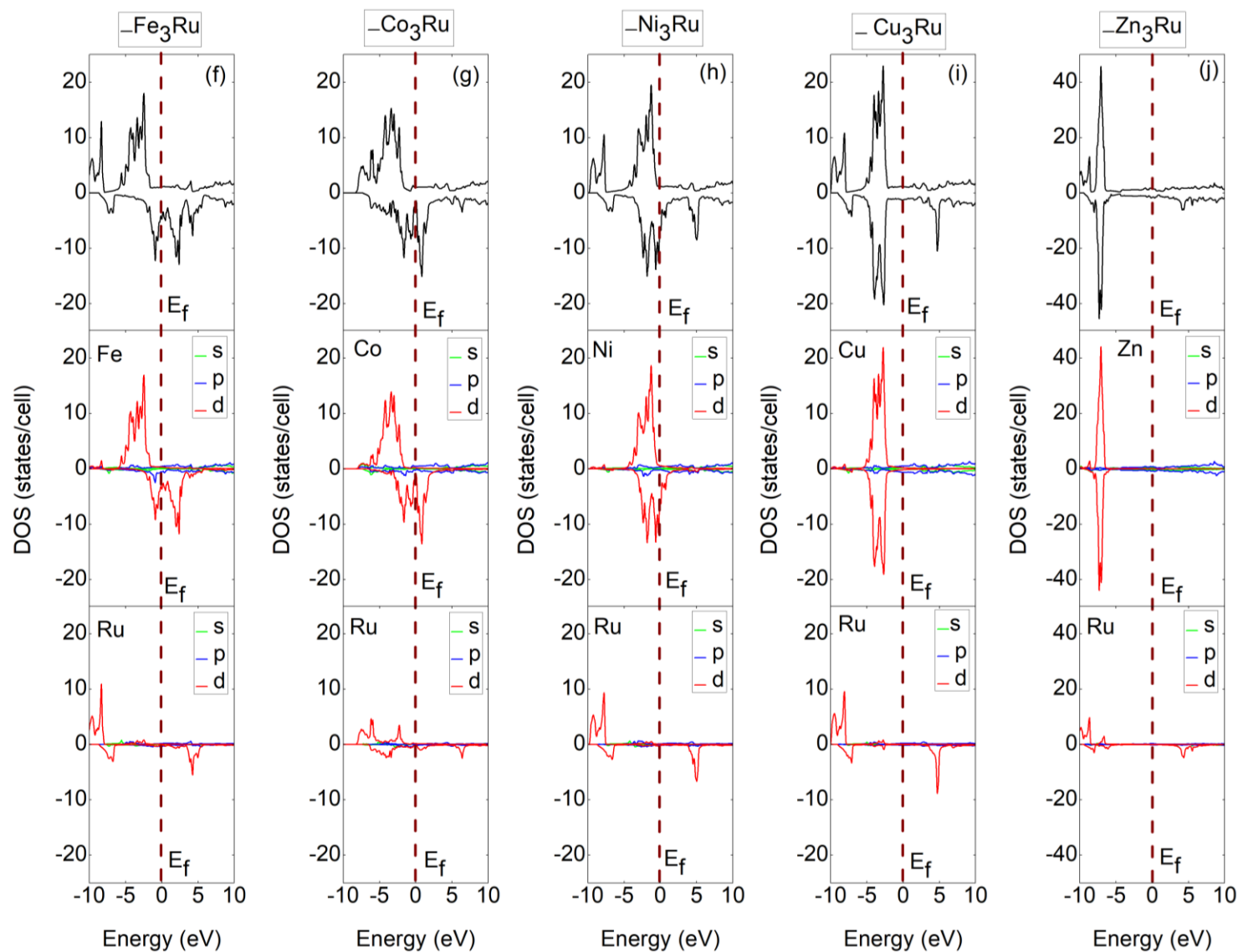


Figure 4.5 (b): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary A15 3d- X_3 Ru transition ($X = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn) calculated from GGA functional. Fermi energy is set to zero in each compound.

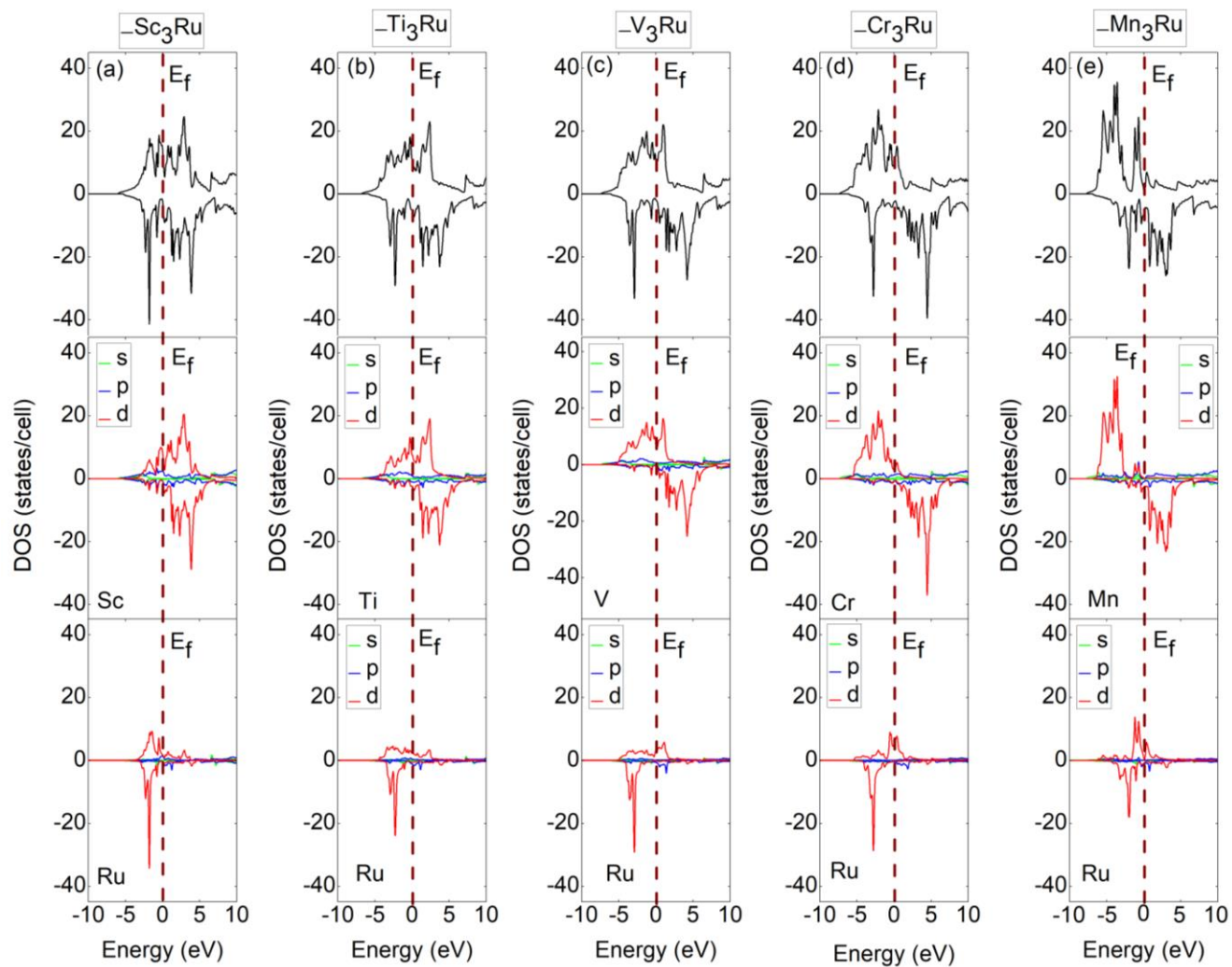


Figure 4.6 (a): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary D0c 3d- X_3 Ru transition metal ($X = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}$ and Mn) calculated from GGA functional. Fermi energy is set to zero in each compound.

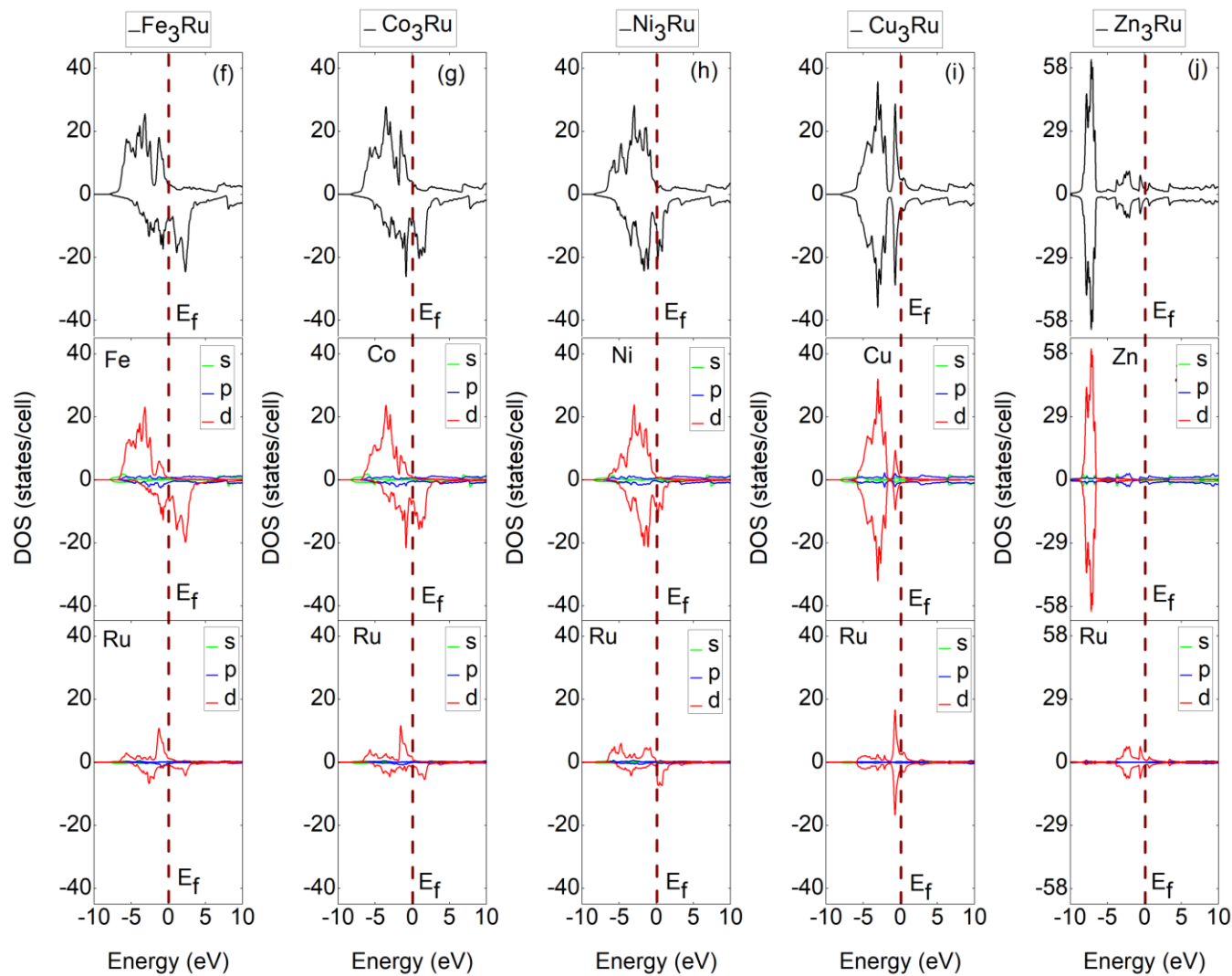


Figure 4.6 (b): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary D0c 3d- X_3 Ru transition metal ($X = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn) calculated from GGA functional. Fermi energy is set to zero in each compound. The arrows represent the spin up and down DOS. All the alloys have the same vertical scale except Zn_3Ru .

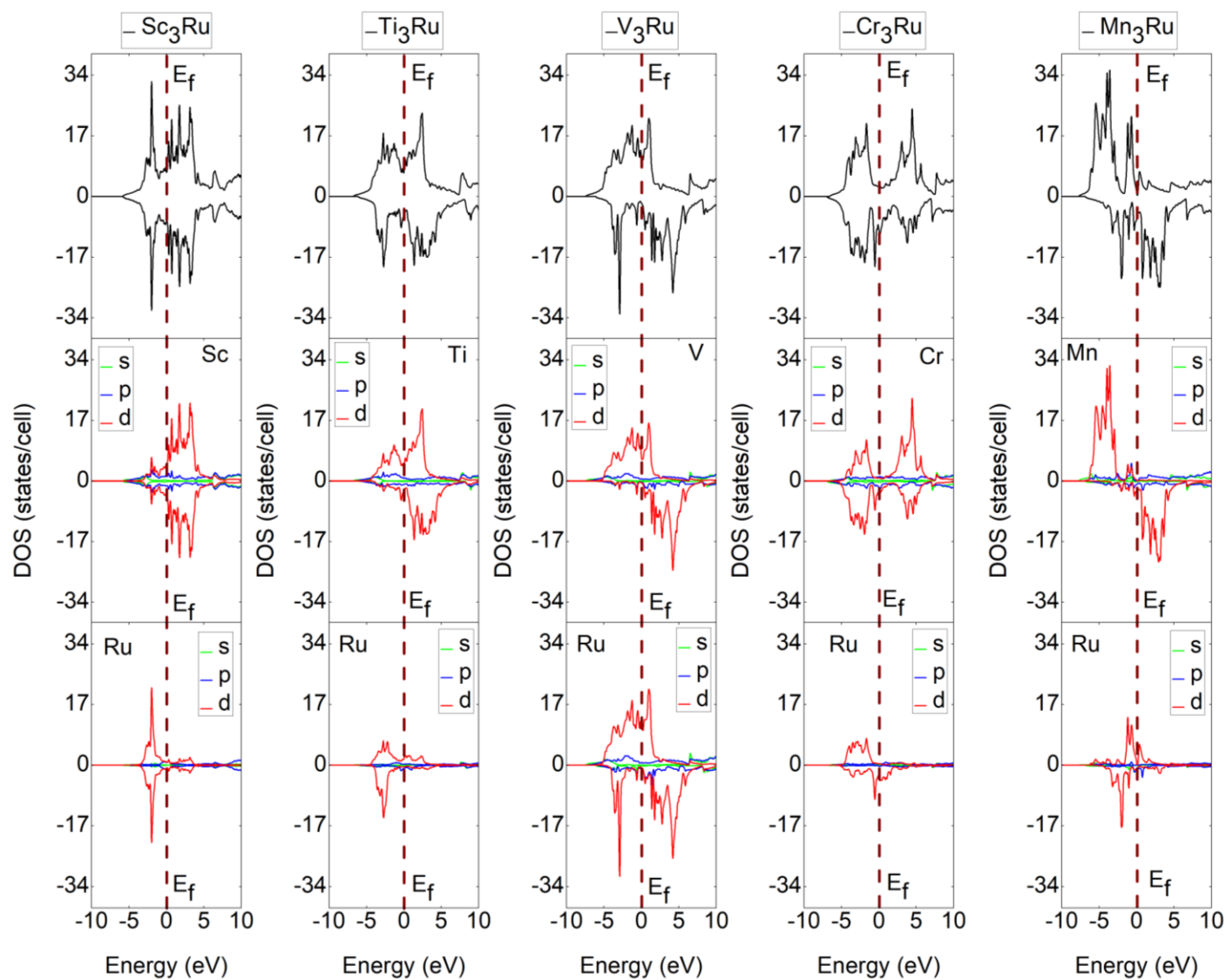


Figure 4.7 (a): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary tP16 3d- X_3 Ru transition metal ($X = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}$ and Mn) calculated from GGA functional. Fermi energy is set to zero in each compound.

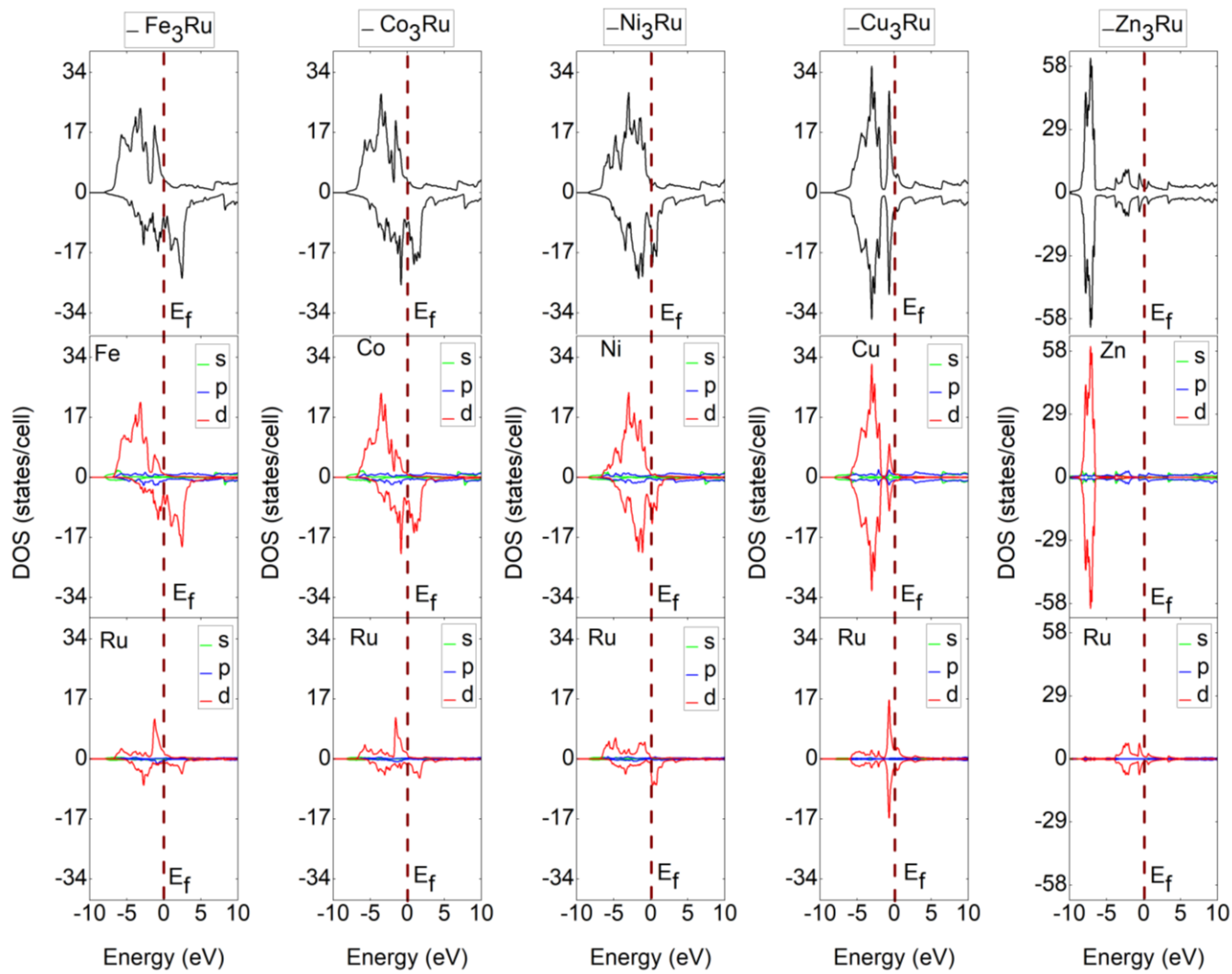


Figure 4.7 (b): Spin polarized total density of states (DOS) and partial density of states (PDOS) of binary tP16 3d- X_3 Ru transition metal ($X = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn) calculated from GGA functional. Fermi energy is set to zero in each compound. All the alloys have the same vertical scale except Zn_3Ru .

4.4.2 Metallic characteristics and conductivity

In the A15 phase, the total density of states (TDOS) plots for $X_3\text{Ru}$ alloys, with $X = \text{Sc, Ti, V, Cr,}$ and Mn , demonstrate a clear overlap between the valence and conduction bands at the Fermi level. This overlap is a strong indication of metallic behavior, which correlates with enhanced electrical conductivity in these alloys. In contrast, alloys with $X = \text{Fe, Co, Ni, Cu,}$ and Zn show significantly weaker metallic characteristics. This reduction in metallic behavior can be attributed to a diminished density of states in the conduction region of the spin-up bands.

In the D0c phase, the TDOS plots for $X_3\text{Ru}$ alloys with $X = \text{Sc, Ti, V, Cr, Fe, Co,}$ and Ni again reveal a robust overlap between the valence and conduction bands at E_F , attributed to their high density of states. Like the A15 phase, this overlap suggests that these alloys act as effective metallic conductors. However, distinct differences arise in the behavior of alloys such as $\text{Mn}_3\text{Ru, Cu}_3\text{Ru,}$ and Zn_3Ru which exhibit a considerably weaker metallic nature, linked to a reduced number of states in the spin-up conduction bands. As a result, these alloys also present lower electrical conductivity in comparison. In the tP16 phase, the TDOS profiles for $\text{Sc}_3\text{Ru, Ti}_3\text{Ru,}$ and V_3Ru illustrate a pronounced overlap between the valence and conduction bands at E_F , further signifying metallic behavior and enhanced electrical conductivity. Conversely, alloys with $X = \text{Cr, Mn, Fe, Co, Ni, Cu,}$ and Zn exhibit weaker metallic characteristics. This reduced conductivity is a consequence of the diminished number of available states in the spin-up conduction bands, leading to lower overall electrical conduction.

Across the three phases, it is observed that there is a significant leftward shift of electronic states from the conduction band to the valence band along the 3d series from Sc_3Ru to Zn_3Ru alloys. This observed shift can be correlated with thermal excitation, a phenomenon where lattice vibrations provide sufficient energy to promote electrons to higher energy bands. As a result, the robust metallic character of these alloys transitions to a more subdued metallic nature throughout the series.

In summary, the analysis of TDOS across different alloy phases highlights the significant influence of electronic structure on the metallic behavior and electrical conductivity of $X_3\text{Ru}$ alloys. Alloys

with a more substantial overlap between the valence and conduction bands generally exhibit stronger metallic characteristics, while those with constrained states in the conduction bands present diminished electrical conductivity. Future research could focus on modifying the composition and structure of these alloys to enhance their electrical properties.

4.4.3 Hybridization and bonding characteristics

In the A15 phase, it is observed that the density of states at the Fermi energy level is reduced in the Cr₃Ru, Mn₃Ru, Zn₃Ru, Cu₃Ru, Ni₃Ru, Co₃Ru, and Fe₃Ru alloys. Similarly, in the D0c phase, the density of states at the Fermi energy level is lower in the Mn₃Ru, Cu₃Ru, and Zn₃Ru alloys. In the tP16 phase, a decreased density of states at the Fermi level is noted for the Cr₃Ru, Mn₃Ru, and Zn₃Ru alloys. This phenomenon suggests covalent bonding characteristics within these alloys [254,255]. The observed low density of states around the Fermi energy level can be attributed to strong hybridization between the X-d orbitals and Ru-d orbitals, resulting in the separation of bonding states from the antibonding states. It is crucial to highlight that the alloys exhibiting a lower density of states at the Fermi level are associated with a lower heat of formation, indicating a greater thermodynamic stability. Therefore, it can be concluded that the stability of the X-Ru alloys is strongly correlated with the magnitude and position of the DOS at the Fermi energy $N(E_f)$ [256–258]. Specifically, a lower $N(E_f)$ is indicative of a more stable phase, underscoring the importance of electronic structure in determining the thermodynamic properties of these materials.

4.5 Mechanical properties

Mechanical properties encompass the macroscopic characteristics of materials that enable them to withstand deformation and fracture under external forces. They describe how materials behave and respond when subjected to various loads and stresses. These properties play a crucial role in determining a material's suitability for specific engineering applications. The mechanical behavior of a solid is influenced by its elastic properties. Elastic constants play a crucial role in various practical applications related to the mechanical properties of materials, including microcracks, stress and strain. Mechanical properties quantify the resistance of crystals to external stress or

strain. This resistance is evaluated by applying a minimal strain to the unit cell, allowing determination of the total energy difference [259,260]. The elastic strain (U) is calculated as

$$U = \frac{\Delta E}{V_0} \frac{1}{2} \sum_i^6 \sum_j^6 C_{ij} e_i e_j \quad (4.3)$$

where ΔE is the change in total energy change of the deformed unit cell relative to the initial cell, V_0 is the unstrained volume, C_{ij} ($i, j = 1$ to 6) are the elastic constants and e_i or e_j corresponds to the strain. In this study, the stress-strain method based on Hook's law was used to calculate the elasticity and the elastic stiffness tensors, expressed as [261]

$$\{\sigma_{ij}\} = [C_{ij}] \{\epsilon_{ij}\} \quad (4.4)$$

where $\{\sigma_{ij}\}$ and $\{\epsilon_{ij}\}$ are the stress and strain tensors respectively.

In this study, we specifically use independent elastic constants C_{ij} to describe the mechanical resistance of X_3Ru alloys in the A15, D0c and tP16 phases under applied external stresses. Elastic constants serve as the basis for analyzing the mechanical properties of these alloys including bulk modulus, shear modulus, Young's modulus, bulk to shear ratio, Poisson's ratio, Vickers hardness, anisotropic factors and melting temperatures. These parameters are crucial for evaluating the suitability of materials for high-temperature structural applications.

4.5.1 Elastic constants

Elastic constants are fundamental physical properties that characterize how a material reacts to external forces and deformation. Accurate calculations of these constants are vital for a thorough understanding of solid mechanics. Different crystal structures exhibit distinct configurations of independent elastic constants; for example, cubic, tetragonal, orthorhombic, and monoclinic crystals are characterized by their own respective sets of constants: (C_{11} , C_{12} , C_{44}) for cubic; and (C_{11} , C_{12} , C_{33} , C_{44} , C_{66}) for tetragonal systems. This study focuses specifically on the cubic and

tetragonal elastic constants, which are pertinent to the crystal structures of A15, D0c, and tP16 X₃Ru alloys.

The crystal structure of A15 X₃Ru is cubic, as illustrated in Figure 4.1. For cubic systems to exhibit mechanical stability, they must satisfy the following conditions, known as Born-Huang conditions [262,263].

$$C_{44} > 0; C_{11} > C_{12}; C_{11} + 2C_{12} > 0 \quad (4.5)$$

For tetragonal D0c and tP16 X₃Ru alloys, the criteria for mechanical stability criteria at zero temperature and pressure are defined by the following set of equations [264]:

$$\begin{aligned} (C_{11} + C_{33} - 2C_{13}) > 0; (C_{11} - C_{12}) > 0 \\ C_{11} > 0; C_{33} > 0; C_{44} > 0; C_{66} > 0 \\ (2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0 \end{aligned} \quad (4.6)$$

Table 4.6 presents the calculated elastic constants of transition metal cubic A15 X₃Ru alloys. Among these, only the elastic constants of Cr₃Ru and Sc₃Ru satisfies the Born-Huang criteria given in equation 4.5, whereas the rest of the other structures do not, which is attributed to $C_{44} < 0$ and $C_{12} < 0$. For cubic systems, the elastic constant C_{11} defines the linear compression resistance of a material [265], while, C_{44} reflects the degree of shear resistance in the (100) plane and which affects the hardness of solid materials indirectly [266].

The elastic constant C_{11} ranges from 78 GPa for Sc₃Ru to 1328 GPa for Fe₃Ru. In contrast, the elastic constant C_{44} ranges from -621 GPa for V₃Ru to 137 GPa for Fe₃Ru. In this context, Ti₃Ru demonstrates the highest compressibility resistance evidenced by its significant C_{11} value of 1061 GPa [267]. The order of increasing elastic constant C_{11} is as follows: Sc₃Ru < Zn₃Ru < Ni₃Ru < Mn₃Ru < Cu₃Ru < V₃Ru < Cr₃Ru < Co₃Ru < Ti₃Ru < Fe₃Ru. Additionally, Fe₃Ru exhibits a higher C_{44} value of 137 GPa, suggesting a stronger capability to withstand shear distortion in (100) plane.

The order of increasing elastic constant C_{44} is as follows: $V_3Ru < Co_3Ru < Ni_3Ru < Cu_3Ru < Ti_3Ru < Zn_3Ru < Mn_3Ru < Cr_3Ru < Sc_3Ru < Fe_3Ru$.

Tables 4.7 and 4.8 present the calculated elastic constants of tetragonal D0c and tP16 X_3Ru alloys. In the D0c phase, it is found that the elastic constants of V_3Ru , Cr_3Ru , Mn_3Ru , Co_3Ru , Ni_3Ru , Cu_3Ru , and Zn_3Ru satisfy the Bohr-Huang mechanical stability criteria given in equation 4.6 whilst, Sc_3Ru , Ti_3Ru and Fe_3Ru does not due to $C_{44} < 0$ and $C_{66} < 0$. Furthermore, the tP16 X_3Ru ($X = V, Cr, Mn, Co, Ni, Cu$ and Zn) alloys demonstrate mechanical stability, indicating that these alloys can withstand mechanical stress without transitioning to unstable phases. An alloy's ability to withstand mechanical stress without collapsing is governed by its elastic constants, which are determined by atomic bonding and electronic structure. Alloys that satisfy the Bohr-Huang criteria are mechanically stable, whereas those that fail are unstable. This highlights how quantum-level bonding interactions manifest as macroscopic mechanical resilience.

For tetragonal structures, the elastic constants C_{11} and C_{33} describe the linear compression resistance along the x and z directions under applied stress [265]. The elastic constants C_{11} and C_{33} range is as follows: for C_{11} : 78 GPa (Cr_3Ru) to 352 GPa and (Fe_3Ru) whilst for C_{33} : the range starts from 55 GPa (Cr_3Ru) to 282 GPa (Ni_3Ru). In this context, the D0c alloys of V_3Ru , Mn_3Ru , Fe_3Ru , Co_3Ru , Ni_3Ru , Cu_3Ru and Zn_3Ru exhibit the largest C_{11} and C_{13} elastic constants, indicating that they are incompressible under uniaxial stress along x and z directions. whereas Sc_3Ru , Ti_3Ru and Cr_3Ru alloys exhibit the lowest C_{11} and C_{13} elastic constants. Notably, C_{11} is found to be larger than C_{33} for all the studied compounds, signifying that the incompressibility along the x-axis in these alloys is superior to that along the z-axis.

The order of increasing elastic constant C_{11} is: $Cr_3Ru < Sc_3Ru < Ti_3Ru < Mn_3Ru < V_3Ru < Zn_3Ru < Cu_3Ru < Ni_3Ru < Co_3Ru < Fe_3Ru$ whereas for C_{33} : $Cr_3Ru < Sc_3Ru < Ti_3Ru < Mn_3Ru < V_3Ru < Cu_3Ru < Zn_3Ru < Co_3Ru < Fe_3Ru < Ni_3Ru$. Table 4.8 presents the elastic constants for the tP16 X_3Ru alloys. In the tP16 phase, the elastic constant C_{11} ranges from 52 GPa for Cr_3Ru to 361 GPa for Fe_3Ru , while C_{33} starts from 5 GPa for Cr_3Ru to 286 GPa for Ni_3Ru . The calculated C_{11} and C_{33} values for all alloys surpass those of other elastic constants, indicating strong resistance to compression under uniaxial stress along the x and z-axis.

Table 4.6: Computed elastic constants (C_{ij}), average elastic moduli of bulk modulus B, shear modulus G and Young's modulus E in Voigt, Reuss and Hill approximation for A15 X_3Ru compounds. All elastic constants and modulus are in GPa.

A15 structure	C_{11} (GPa)	C_{12} GPa	C_{44} GPa	B_H GPa	G_H GPa	E_H GPa
Sc ₃ Ru	78	104	33	95	-33	-113
Ti ₃ Ru	1061	74	-34	403	58	167
V ₃ Ru	242	95	-621	144	-60	-209
Cr ₃ Ru	336	245	4	275	14	40
Mn ₃ Ru	145	48	-4	80	5	14
Fe ₃ Ru	1328	-922	137	1060	209	672
Co ₃ Ru	765	120	-340	335	-991	-220000
Ni ₃ Ru	91	102	-163	98	-57	-210
Cu ₃ Ru	156	54	-43	88	-85	-374
Zn ₃ Ru	79	40	-19	53	-47	-198

Similar to the D0c phase, we observe that C_{11} significantly exceeds C_{33} across all tP16 structures, further reinforcing their high resistance to compression along the x-axis [265]. The order of increasing elastic constant C_{11} is: Cr₃Ru < Sc₃Ru < Ti₃Ru < Mn₃Ru < V₃Ru < Zn₃Ru < Cu₃Ru < Co₃Ru < Ni₃Ru < Fe₃Ru whereas for C_{33} : Cr₃Ru < Sc₃Ru < Mn₃Ru < V₃Ru < Ti₃Ru < Zn₃Ru < Cu₃Ru < Fe₃Ru < Co₃Ru < Ni₃Ru. Elastic constants quantify how strongly atomic bonds resist compression along specific directions. Larger values indicate stronger, less compressible bonds. Since C_{11} consistently exceeds C_{33} across all alloys, these tetragonal structures are stiffer along the x-axis than the z-axis, revealing how anisotropic bonding at the microscopic level translates into macroscopic mechanical behavior.

The elastic rigidity of a material is described by the combination of the elastic constants C_{11} , C_{12} and C_{33} . When $C_{11} + C_{12} > C_{33}$ the materials are said to be elastically rigid in (001) plane. Notably, all the D0c and tP16 X_3Ru alloys are elastically rigid, with the exception of D0c Cr₃Ru, consistent with previous observations [268]. However, for cubic phase, it is not possible to define the elastic rigidity of these systems and this attributes to $C_{11} = C_{33}$ elastic constants [197]. In tetragonal systems, the elastic constants C_{44} and C_{66} quantify a material's hardness and resistance to tangential shear deformation along the (100) and (001) planes, respectively [269]. The present

calculations indicate that shearing in the $[100](010)$ plane is easier than in the $[100](001)$ plane [270]. Generally, we note that C_{44} is greater than C_{66} in both D0c and tP16-X₃Ru alloys except for Cr₃Ru in tP16 phase, indicating that the shear $[100](001)$ plane is difficult than in the $[100](010)$ plane.

From Table 4.7, it is evident that the D0c Ni₃Ru and Co₃Ru alloys exhibit the highest C_{44} elastic constants of 113 GPa and 112 GPa, respectively. Whilst -5 GPa (Ti₃Ru) alloy has the lowest value. The order of increasing elastic constant C_{44} is: Fe₃Ru < Ti₃Ru < Sc₃Ru < Cr₃Ru < Co₃Ru < Mn₃Ru < Cu₃Ru < Zn₃Ru < V₃Ru < Ni₃Ru. For the elastic constant C_{66} , Ni₃Ru (56 GPa) and V₃Ru (53 GPa) possess the highest C_{66} values whereas, Ti₃Ru (-8 GPa) and Fe₃Ru (-52 GPa) alloys have the least values. The order of increasing elastic constant C_{66} is: Fe₃Ru < Ti₃Ru < Sc₃Ru < Cr₃Ru < Mn₃Ru < Cu₃Ru < Co₃Ru < V₃Ru < Zn₃Ru < Ni₃Ru.

In the tP16 phase, Ti₃Ru and Co₃Ru alloys demonstrate the highest C_{44} elastic constants of 155 GPa and 131 GPa, respectively whilst, Cr₃Ru (-3 GPa) and Sc₃Ru (38 GPa) have the least values. The order of increasing elastic constant C_{44} is: Cr₃Ru < Sc₃Ru < Fe₃Ru < V₃Ru < Mn₃Ru < Zn₃Ru < Cu₃Ru < Ni₃Ru < Co₃Ru < Ti₃Ru. For the elastic constant C_{66} , Ni₃Ru (63 GPa) and Zn₃Ru (53 GPa) possess the highest C_{66} values whereas, Fe₃Ru (-42 GPa) and Ti₃Ru (4 GPa) alloys have the least values. On the other hand, Ni₃Ru and Zn₃Ru have the highest C_{66} elastic constant in both D0c and tP16 phases, indicating that these alloys may possess high hardness characteristics. The order of increasing elastic constant C_{66} is: Fe₃Ru < Ti₃Ru < Sc₃Ru < Cr₃Ru < Mn₃Ru < Cu₃Ru < Co₃Ru < V₃Ru < Zn₃Ru < Ni₃Ru. Elastic constants provide a direct measure of how atomic bonds resist compression and shear along different directions. Higher values reflect stronger, less compressible bonds. The consistent observation that C_{44} exceeds C_{66} in these tetragonal alloys indicates they are more resistant to shear in one plane than another, showing how microscopic bonding anisotropy translates into macroscopic rigidity and directional hardness.

4.5.2 Bulk, Shear and Young's moduli

The bulk modulus, shear modulus, and Young's modulus are three fundamental measures of a material's elasticity, each describing different types of deformation behavior under applied forces. An understanding of these moduli not only aids in material selection for engineering applications

but also facilitates the design of structures and components that can effectively withstand the forces they encounter in real-world scenarios. This section presents a discussion of the results obtained in this study regarding the bulk modulus, shear modulus, and Young's modulus of X₃Ru alloys in the A15, D0c, and tP16 crystallographic phases.

4.5.2.1 Bulk modulus

The Bulk modulus reflects a material's response to uniform compression, reflecting its capacity to resist changes in volume under applied pressure. For cubic A15 crystal structures, B is defined as

$$B = B_H = \left(\frac{B_V + B_R}{2} \right) \quad (4.7)$$

where,

$$B = B_H = B_V = \left(\frac{C_{11} + 2C_{12}}{3} \right) \quad (4.8)$$

with B_R, B = B_H and B_V being the Bulk modulus for Reuss, Voigt and Hill approximations [271,272].

Table 4.7: Computed elastic constants (C_{ij}), Shear moduli (C'), average elastic moduli of bulk modulus B, shear modulus G and Young's modulus E in Voigt, Reuss and Hill approximation for D0c X₃Ru compounds. All elastic constants and moduli are reported in GPa.

D0c	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	B _H	G _H	E _H
	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa	GPa
Sc ₃ Ru	96	34	69	61	34	-7	66	1	3
Ti ₃ Ru	111	86	104	69	-5	-8	98	-7	-21
V ₃ Ru	200	30	62	147	92	53	95	70	169
Cr ₃ Ru	78	-36	16	55	55	0.8	22	20	46
Mn ₃ Ru	175	17	77	130	78	27	91	50	126
Fe ₃ Ru	353	40	113	272	37	-52	168	73	192
Co ₃ Ru	340	82	181	230	112	25	200	64	174
Ni ₃ Ru	326	111	167	282	113	56	203	84	222
Cu ₃ Ru	258	91	171	195	94	29	175	45	125
Zn ₃ Ru	256	73	120	219	92	37	151	67	176

For tetragonal D0c and tP16 X₃Ru alloys, the Bulk modulus in Voigt (V), Reuss (R) and Hill (H) approximations [271,272] is defined as follows.

$$B_H = B_V + B_R \quad (4.9)$$

$$B_V = \frac{1}{9}(2C_{11} + C_{12}) + C_{33} + 4C_{13} \quad (4.10)$$

and the Reuss bounds are:

$$B_R = \frac{C^2}{M} \quad (4.11)$$

where

$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13} \quad (4.12)$$

In Tables 4.6-4.8, we present the calculated bulk (B) modulus, shear (G) modulus, and Young's modulus for the A15, D0c and tP16 X₃Ru alloys (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn). In the A15 phase, the calculated values of the bulk modulus vary significantly, ranging from 53 GPa for Zn₃Ru to 1060 GPa of Fe₃Ru. The trend observed in the moduli is: Zn₃Ru < Mn₃Ru < Cu₃Ru < Sc₃Ru < Ni₃Ru < V₃Ru < Cr₃Ru < Co₃Ru < Ti₃Ru < Fe₃Ru, notably with each alloy exhibiting a positive bulk modulus.

While most of the calculated bulk modulus fall within the range of 0 - 403 GPa, Fe₃Ru exhibits the highest bulk modulus (1060 GPa) which exceeds the typical range. This exceptional value can be explained in terms of its unique elastic constants (see Table 4.6) discussed above. The elevated bulk modulus of Fe₃Ru indicates its superior ability to resist fracture compared to other A15-X₃Ru alloys, highlighting its potential for applications requiring high structural integrity. The resistance of these alloys to uniform compression is governed by the strength of their atomic bonding. The exceptionally high bulk modulus of Fe₃Ru reflects strong interatomic forces, whereas the much lower values in alloys such as Zn₃Ru indicate weaker bonding.

Table 4.8: Computed elastic constants (C_{ij}), average elastic moduli of bulk modulus B, shear modulus G and Young's modulus E in Voigt, Reuss and Hill approximation for tP16 X_3Ru compounds. All elastic constants and moduli are reported in GPa

tP16 Structure	C_{11} GPa	C_{12} GPa	C_{13} GPa	C_{33} GPa	C_{44} GPa	C_{66} GPa	B_H GPa	G_H GPa	E_H GPa
Sc ₃ Ru	120	65	62	95	38	8	79	23	63
Ti ₃ Ru	172	77	92	162	155	4	114	47	83
V ₃ Ru	193	24	74	154	59	48	98	56	141
Cr ₃ Ru	52	36	53	5	-3	16	45	-7	-21
Mn ₃ Ru	191	29	84	131	78	25	101	50	128
Fe ₃ Ru	361	78	141	238	39	-42	186	72	191
Co ₃ Ru	331	69	170	270	131	36	194	81	213
Ni ₃ Ru	337	115	166	286	117	63	206	90	235
Cu ₃ Ru	262	87	154	192	95	29	167	54	146
Zn ₃ Ru	248	68	122	178	89	53	144	64	168

This illustrates how bonding interactions manifest as macroscopic mechanical stiffness and stability. In the D0c phase, the bulk modulus values vary significantly, ranging from 22 GPa for Cr₃Ru to 203 GPa for Ni₃Ru. Overall, the bulk modulus follows this increasing order: Cr₃Ru < Sc₃Ru < Mn₃Ru < V₃Ru < Ti₃Ru < Zn₃Ru < Fe₃Ru < Cu₃Ru < Co₃Ru < Ni₃Ru, with each of these alloys exhibiting a positive bulk modulus. Similarly, in the tP16 phase, the bulk modulus values range from 45 GPa for Cr₃Ru to 206 GPa for Ni₃Ru, with the sequence of increasing bulk modulus as follows: Cr₃Ru < Sc₃Ru < V₃Ru < Mn₃Ru < Ti₃Ru < Zn₃Ru < Cu₃Ru < Fe₃Ru < Co₃Ru < Ni₃Ru. The capacity of these alloys to resist uniform compression is determined by the strength of their atomic bonding. Alloys with higher bulk moduli, such as Fe₃Ru and Ni₃Ru, possess stronger interatomic forces and are less compressible, whereas alloys with lower values, like Cr₃Ru and Zn₃Ru, are more easily compressed. This underscores how bonding interactions directly manifest macroscopic mechanical stiffness and stability.

It is noteworthy that the trends and magnitudes of the calculated bulk modulus in both the D0c and tP16 phases are closely aligned (see Fig. 4.14), which can be attributed to their similar crystallographic structures. Our calculated bulk modulus for A15, D0c and tP16 phases are comparable to the widely used L1₂-Ni₃Al alloy (173.9 GPa) [273]. Among the alloys which have

been considered in the current study, D0c Ni₃Ru (203 GPa) exhibits the highest bulk modulus, indicating that it possesses the greatest resistance to fracture within the D0c-X₃Ru alloy family. The resistance of these alloys to uniform compression is shaped by both atomic bonding strength and crystal structure. The close alignment of bulk moduli in the D0c and tP16 phases reflects their structural similarity, while the exceptionally high modulus of Ni₃Ru highlights its superior bonding strength and fracture resistance. This demonstrates how bonding interactions directly manifest as macroscopic mechanical stiffness and durability.

4.5.2.2 Shear modulus

The shear modulus (G) describes a material's response to shear stress, which leads to angular distortion without a change in volume. The shear modulus determines a material's stiffness. For cubic A15 structures, G can be expressed as:

$$G = G_H = \left(\frac{G_V + G_R}{2} \right) \quad (4.13)$$

where the G_R and G_V are the Reuss and Voigt bounds [271,272],

$$\text{with } G_V = \left(\frac{C_{11} - C_{12} + 3C_{44}}{5} \right) \quad (4.14)$$

$$\text{and } G_R = \left(\frac{5(C_{11} - C_{12})C_{44}}{(4C_{44} + 3(C_{11} - C_{12}))} \right) \quad (4.15)$$

For tetragonal systems D0c and tP16 systems, shear modulus is calculated as:

$$G_V = \frac{1}{30} (M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}) \quad (4.16)$$

$$G_R = 15 \left[\left(\frac{18B_V}{C^2} \right) + \left(\frac{6}{C_{11} - C_{12}} \right) + \left(\frac{6}{C_{44}} \right) + \left(\frac{3}{C_{66}} \right) \right]^{-1} \quad (4.17)$$

$$\text{where } C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2$$

The evaluation of shear modulus across different phases of Ru-based alloys reveals significant variations, emphasizing their mechanical properties and potential applications. In the A15 phase, the calculated shear modulus values range from -991 GPa for Co₃Ru to 209 GPa for Fe₃Ru. Generally, the shear modulus trends for different alloys can be summarized as follows: Co₃Ru < Cu₃Ru < V₃Ru < Ni₃Ru > Zn₃Ru > Sc₃Ru < Mn₃Ru < Cr₃Ru < Ti₃Ru < Fe₃Ru. The shear modulus for most of these alloys is positive; however, Sc₃Ru, Co₃Ru, Ni₃Ru, Cu₃Ru and Zn₃Ru exhibit negative values. The presence of a significantly negative shear modulus in Co₃Ru (-991 GPa) is particularly noteworthy, as it is linked to its anomalous elastic constant C₄₄ (see Table 4.6). In contrast, Fe₃Ru (209 GPa) demonstrates the highest shear modulus within this phase, suggesting it possesses the greatest resistance to shear stress among the studied A15-X₃Ru alloys. The shear modulus reflects how atomic bonds resist shape deformation. Positive values indicate stable, rigid bonding, while negative values signal lattice instability. The exceptionally high shear modulus of Fe₃Ru demonstrates strong resistance to shear stress, whereas the large negative value in Co₃Ru reveals structural weakness. This highlights how bonding interactions directly manifest as mechanical stability or instability under shear.

In the D0c phase, the shear modulus values range from -7 GPa for Ti₃Ru to 84 GPa for Ni₃Ru, which follows the order: Ti₃Ru < Sc₃Ru < Cr₃Ru < Cu₃Ru < Mn₃Ru < Co₃Ru < Zn₃Ru < V₃Ru < Fe₃Ru < Ni₃Ru. Like the A15 phase, the D0c also exhibits negative shear modulus, further reflecting the instability associated with certain alloys, particularly Ti₃Ru. In the tP16 phase, shear modulus values again demonstrate variability, ranging from -7 GPa for Cr₃Ru to 90 GPa for Ni₃Ru, with the following trend: Cr₃Ru < Sc₃Ru < Ti₃Ru < Mn₃Ru < Cu₃Ru < V₃Ru < Zn₃Ru < Fe₃Ru < Co₃Ru < Ni₃Ru. The negative shear modulus in these alloys indicate potential instability associated with phase transitions, aligned with concepts from Landau theory [274], which postulates that negative elastic moduli may arise due to strain energy functions that exhibit two local minima. While these alloys demonstrate instability, the application of sufficient constraints can stabilize materials with negative elastic moduli.

Moreover, the calculated shear modulus values for the A15, D0c, and tP16 phases are comparable to the well-characterized L1₂-Ni₃Al alloy, which has a shear modulus of 77.8 GPa [275]. Among the D0c and tP16 phases, Ni₃Ru (84 GPa and 90 GPa) consistently shows the highest shear

modulus, reinforcing its superior resistance to shear stress and identifying it as a candidate for applications requiring enhanced mechanical stability. In conclusion, the trends in shear modulus across the various phases of Ru-based alloys highlight both their mechanical characteristics and the influence of phase stability. The presence of negative shear modulus values in several alloys indicates underlying instability, which could have implications for the design and utilization of these materials in practical applications. Further investigation into the stabilization of these alloys and their performance in applied settings could provide deeper insights into their mechanical behavior and potential applications in advanced materials science.

4.5.2.2 Young's modulus

Young's modulus represents the tensile elasticity of a material, indicating its ability to deform linearly under axial tensile or compressive forces. Specifically, Young's modulus [276] describes the material's response to strain due to uniaxial stress. Higher values of Young's modulus signify a stiffer material, making it crucial parameter in assessing a material's stiffness. Unlike the Bulk modulus and shear modulus, Young's modulus is independent of the type of crystal structure of a material. It is Mathematically expressed as:

$$E = \left(\frac{9B_H G_H}{3B_H + G_H} \right), \quad (4.18)$$

where B and G are the Bulk and Shear moduli, respectively. Table 4.6-4.8 shows the calculated Young's moduli (E) for A15, D0c and tP16-X₃Ru (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) alloys. The analysis of the calculated Young's moduli for A15, D0c and tP16 X₃Ru alloys reveals important trends in the mechanical properties of these materials. In the A15 phase, the Young's modulus values exhibit a considerable range, from -220000 GPa for Co₃Ru to 672 GPa for Fe₃Ru. Generally, the observed trend of increasing Young's moduli is: Co₃Ru < Cu₃Ru < Ni₃Ru < V₃Ru < Zn₃Ru < Sc₃Ru < Mn₃Ru < Cr₃Ru < Ti₃Ru < Fe₃Ru. The significant stiffness of Fe₃Ru, indicated by its higher Young's modulus, suggests that it is one of the strongest materials within this phase, while Co₃Ru is identified as the least stiff. This relationship between stiffness and strength implies that higher values of Young's modulus correlate positively with increased material strength.

Notably, the negative Young's modulus values for Cu_3Ru , Co_3Ru , Ni_3Ru and Zn_3Ru can be explained in terms of its elastic constants (detailed in Table 4.6). The negative Young's modulus signal a potential instability associated with phase transitions, similar to the phenomena observed in ferro-elastic phase transformation [277]. According to Landau theory [274], this negative elastic modulus arises when two local minima are established in the strain energy function. However, it is possible to stabilize solids by exhibiting negative elastic moduli through sufficient constraint. In the D0c phase, Young's modulus ranges from -21 GPa for Ti_3Ru to 222 GPa for Ni_3Ru , following the trend: $\text{Ti}_3\text{Ru} < \text{Sc}_3\text{Ru} < \text{Cr}_3\text{Ru} < \text{Cu}_3\text{Ru} < \text{Mn}_3\text{Ru} < \text{V}_3\text{Ru} < \text{Co}_3\text{Ru} < \text{Zn}_3\text{Ru} < \text{Fe}_3\text{Ru} < \text{Ni}_3\text{Ru}$. In the tP16 phase Young's modulus ranges from -21 GPa for Cr_3Ru to 235 GPa for Ni_3Ru , following the trend: $\text{Cr}_3\text{Ru} < \text{Sc}_3\text{Ru} < \text{Ti}_3\text{Ru} < \text{Mn}_3\text{Ru} < \text{V}_3\text{Ru} < \text{Cu}_3\text{Ru} < \text{Zn}_3\text{Ru} < \text{Fe}_3\text{Ru} < \text{Co}_3\text{Ru} < \text{Ni}_3\text{Ru}$. Ni_3Ru again stands out with the highest stiffness in the D0c and tP16 phases, reinforcing its position as a significant material in this analysis.

The Young's modulus values obtained for the A15, D0c, and tP16 phases show strong agreement with those of the widely used $\text{L1}_2\text{-Ni}_3\text{Al}$ alloy, which has a Young's modulus of 203.1 GPa [275]. Upon comparing the bulk modulus, shear modulus and Young's modulus for all the A15- X_3Ru alloys, Fe_3Ru consistently outperforms other alloys in terms of these properties. In contrast, within the D0c- X_3Ru alloys, the Ni_3Ru system exhibits superior performance, characterized by the highest values in bulk, shear, and Young's moduli. This superior performance reflects its enhanced ability to withstand compression, resist shear distortion, and maintain overall stiffness. In the tP16- X_3Ru series, Ni_3Ru 's exceptional shear modulus and Young's modulus further illustrate its resistance to shear distortion and overall stiffness among the tested alloys. These outstanding mechanical properties highlight the potential applicability of these materials in high-temperature structural applications.

In conclusion, the careful examination of the calculated Young's moduli reveals critical insights into the mechanical stability and strength of various metal alloys. Such information is vital for future innovations in materials science and engineering, particularly in contexts where structural integrity under varying conditions is paramount.

4.5.2.3 Bulk to Shear ratio

The ratio of the bulk modulus to the shear modulus (B_H/G_H) of materials serves as a predictive tool for their ductility or brittleness. This ratio reflects the balance between two competing processes: plasticity and fracture. When plasticity is more dominant, the material tends to be ductile; conversely, when fracture prevails, the material tends to be brittle [278]. Ductility is defined as the capacity of a material to undergo plastic deformation prior to failure. This property is crucial in material engineering, particularly for components that require flexibility and resilience under stress. In contrast, brittle materials pose significant risks in structural applications due to their tendency to fracture suddenly under stress or defects [240]. Among the various models which have been developed to predict material ductility, the bulk-to-shear ratio (B_H/G_H) proposed by Pugh [278], is widely used.

According to this criterion, a critical threshold value of approximately 1.75 separates ductile from brittle behavior. Specifically, if $B/G > 1.75$, the material is considered ductile; if it is less than or equal to this value, the material is deemed brittle. The Pugh criterion provides a straightforward and quantifiable method for assessing the performance characteristics of materials, particularly in design contexts where failure risks must be minimized.

The Pugh's ratio has been widely used in assessment of the bulk-to-shear ratio for a wide range of materials, including cubic [240,241,250,279–283], hexagonal [284–287], orthorhombic [288–291] and tetragonal [234,236,292,293] systems. While alternative models such as Cauchy pressure $C_p = C_{12} - C_{44}$ [294] and Poisson's ratio [295,296] also evaluate ductility and brittleness, the Pugh criteria remains a prominent indicator of ductility across a broad spectrum of materials. These parameters such as Cauchy pressure and Poisson's ratio have limitations. One often-overlooked factor is geometry, particularly the influence of size and the nature of dislocations, which plays a critical role. Size-dependent effects are evident in indentation experiments, where hardness increases markedly as the indentation depth decreases [42].

Table 4.9: The calculated B/G ratio, melting temperature (T_m) in kelvin, crystal anisotropy (A^U) and hardness (H_V) for A15 phase. UND = undefined due to the negative square root in G_H/B_H (equation 4.13), indicating instability associated with a phase change in these structures.

A15 structure	B_H/G_H	$T_m \pm 300$ K	A^U	H_V
Sc ₃ Ru	-2.9	1013.98	-5.90	UND
Ti ₃ Ru	7.0	6823.51	-19.76	-0.77
V ₃ Ru	-2.4	1983.22	-12.69	UND
Cr ₃ Ru	19.6	2538.76	11.27	-2.7
Mn ₃ Ru	16.0	1409.95	-16.46	-2.8
Fe ₃ Ru	5.1	7295.48	0.05	3.81
Co ₃ Ru	-0.3	5074.15	-85.78	UND
Ni ₃ Ru	-1.7	1090.81	33.03	UND
Cu ₃ Ru	-1.0	1474.96	-4.84	UND
Zn ₃ Ru	-1.1	1019.89	-4.80	UND

Table 4.10: The calculated B/G ratio, melting temperature (T_m) in kelvin, crystal anisotropy (A^U) and hardness (H_V) for D0c phase. UND = undefined due to the negative square root in G_H/B_H (equation 4.13), indicating instability associated with a phase change in these structures.

D0c Structure	B_H/G_H	$T_m \pm 300$ K	A^U	H_V
Sc ₃ Ru	66.2	732.18	-10.64	-3.00
Ti ₃ Ru	-14.1	789.00	-2.997	UND
V ₃ Ru	1.4	1175.82	0.47	13.80
Cr ₃ Ru	1.1	1309.04	44.98	7.32
Mn ₃ Ru	1.8	1073.28	1.69	6.79
Fe ₃ Ru	2.3	1821.44	-2.24	6.28
Co ₃ Ru	3.1	1717.64	3.40	3.01
Ni ₃ Ru	2.4	1756.23	0.60	6.51
Cu ₃ Ru	3.9	1422.20	5.77	0.79
Zn ₃ Ru	2.2	1450.94	0.62	6.05

Table 4.11: The calculated B/G ratio, Cauchy pressure ($C_{12}-C_{44}$), Poisson's ratio (ν), Shear moduli (C'), melting temperature (T_m) in kelvin, crystal anisotropy (A^U) and hardness (H_V) for tP16 phase. UND = undefined due to the negative square root in G_H/B_H (equation 4.13), indicating instability associated with a phase change in these structures.

tP16 Structure	B_H/G_H	$T_m \pm 300$ K	A^U	H_V
Sc ₃ Ru	3.4	858.60	1.86	0.0
Ti ₃ Ru	2.5	1114.49	22.53	3.6
V ₃ Ru	1.8	1163.46	0.35	8.35
Cr ₃ Ru	-6.9	516.68	-4.80	UND
Mn ₃ Ru	2.0	1122.71	1.77	5.6
Fe ₃ Ru	2.6	1794.87	-2.53	5.0
Co ₃ Ru	2.4	1602.33	1.99	6.4
Ni ₃ Ru	2.3	1795.19	0.49	7.5
Cu ₃ Ru	3.1	1428.89	2.68	2.4
Zn ₃ Ru	2.2	1363.19	1.01	5.9

Because the elastic properties remain unchanged, conventional criteria such as the Pugh ratio or Cauchy pressure cannot adequately account for these phenomena [297]. The limitations of Poisson's ratio in material alloys arise primarily from the assumption that the material behaves isotropically and remains linearly elastic. In practice, Poisson's ratio often deviates from these assumptions, particularly within the plastic deformation region. Experimental studies have demonstrated that Poisson's ratio can vary significantly near the yield stress, underscoring the need for more refined material models [298–302]. In this thesis, the Pugh criteria has been specifically applied to analyse the bulk-to-shear modulus ratio (B/G) of the X_3 Ru alloys. The computed bulk to shear ratio results for the A15, D0c and tP16 X_3 Ru alloys are presented in Tables 4.9-4.11. We note that in A15 phase, the alloys Ti₃Ru (7.0), Cr₃Ru (19.6), Mn₃Ru (16.0) and Fe₃Ru (5.1) exhibit ductile behavior.

Similarly, in the D0c and tP16 phases, Sc₃Ru (66.2 and 3.4) Mn₃Ru (1.8 and 3.4), Fe₃Ru (2.3 and 2.6), Co₃Ru (3.1 and 2.4), Ni₃Ru (2.4 and 2.3), Cu₃Ru (3.9 and 3.1), and Zn₃Ru (both = 2.2) alloys display ductility according to the Pugh criteria whilst, other compounds in A15, D0c and tP16 phases are brittle due to $B/G < 1.75$. Our calculated ductility values ($B/G > 1.75$) for the A15, D0c and tP16 phases are comparable to the currently used L1₂-Ni₃Al alloy (2.235) [275]. In the A15 phase, Ti₃Ru, Cr₃Ru, Mn₃Ru and Fe₃Ru exhibit the highest bulk to shear ratios, In D0c phase,

Sc₃Ru and Cu₃Ru alloys exhibit the highest B/G ratio, while in the tP16 phase, Sc₃Ru leads with the highest B/G ratio. The order of increasing B/G ratios of compounds in A15 phase are as follows: Sc₃Ru < V₃Ru < Ni₃Ru < Zn₃Ru < Cu₃Ru < Co₃Ru < Fe₃Ru < Ti₃Ru < Mn₃Ru < Cr₃Ru whilst for D0c phase the B/G ratios are: Ti₃Ru < Cr₃Ru < V₃Ru < Mn₃Ru < Zn₃Ru < Fe₃Ru < Ni₃Ru < Co₃Ru < Cu₃Ru < Sc₃Ru and for tP16 B/G ratios are : Cr₃Ru < V₃Ru < Mn₃Ru < Zn₃Ru < Ni₃Ru < Co₃Ru < Ti₃Ru < Fe₃Ru < Cu₃Ru < Sc₃Ru. These findings suggest that this material can endure significant plastic deformation before fracturing. The B/G ratio serves as a key measure of how alloys respond to applied stress. High ratios signify ductile behavior, allowing the material to undergo substantial plastic deformation before fracture, while low ratios indicate brittleness. This demonstrates how atomic-scale bonding interactions and crystal symmetry directly manifest as macroscopic mechanical resilience or fragility.

4.5.2.4 Vickers hardness test

The Vickers hardness test is a crucial technique for quantifying the hardness of engineering materials, especially those intended for high-temperature applications. This property is vital since it affects a material's resistance to deformation under stress, which is particularly important in demanding environments. For engineering materials to perform effectively at elevated temperatures, they must possess a sufficient level of hardness, a measure of resistance to localized plastic deformation caused by mechanical indentation or abrasion. Since hardness is not a fundamental property, its value can be influenced by various factors, including tensile strength, yield strength, modulus of elasticity, temperature, pressure and porosity.

Experimentally, hardness is tested by pressing an indenter into the sample surface and measuring the dimensions of the resulting indentation [303]. In materials science, materials with Vickers hardness above 40 GPa are classified as superhard [304,305]. Diamond, with a Vickers hardness of 95 GPa, is the hardest known material and possesses the highest shear and Young's moduli. However, its application is limited due to its chemical reactivity with ferrous materials and susceptibility to oxidation.

In recent decades, extensive research has focused on developing new and inert superhard materials for both scientific exploration and practical applications in industries, such as wear-resistant coatings, abrasives, and cutting and polishing tools [306–308]. While there has been significant progress in the experimental synthesis of boron based [309] or carbide based [309–312] or nitride based [311] superhard compounds [307,313–316], these materials lack certain fundamental properties such as high-temperature phase stability, oxidation resistance, and sufficient fracture toughness. which limits their use in high-temperature structural applications [317,318].

Designing hard materials based on atomic arrangements within crystal structures requires reliable models for hardness quantification [319]. The commonly used model is the Vickers hardness test due to its accuracy and reliability in comparison with experimental data across a wide range of materials [303]. In this thesis we use the Vickers hardness test predicted by Chen et.al [320] to calculate the hardness of A15, D0c, tP16 X₃Ru alloys, using equation 4.13:

$$H_V = 2(K^2 G)^{0.585} - 3 \quad (4.19)$$

where K is ratio of the shear to bulk moduli (G/B)

The calculated Vickers hardness (H_V) values of the A15, D0c and tP16-X₃Ru alloys are given in Tables 4.9-4.11. In the A15 phase, Fe₃Ru is predicted to be the hardest alloy with a Vickers hardness of 3.81 GPa. In the D0c phase, V₃Ru has the highest Vickers hardness of 13.80 GPa while, in the tP16 phase V₃Ru again is predicted to be the hardest alloy with the Vickers hardness of 8.35 GPa. Notably, the calculated hardness for certain alloys specifically A15 Sc₃Ru, V₃Ru, Co₃Ru, Ni₃Ru, Cu₃Ru, and Zn₃Ru, along with D0c Ti₃Ru and tP16 Cr₃Ru is undefined. The undefined Vickers hardness arises from to the negative square root in G_H/B_H , indicating instability associated with phase change in these structures. Our hardness results are consistent with other experimental and theoretical data for materials like MgO, ZnTe, InP, LiF, and CrN [303]. However, we also note that our hardness values across the three phases are relatively small, compared to more established materials, such as L1₂-Ni₃Al, which exhibits a hardness of 54 GPa [321]. This disparity might present limitations where hardness is a critical factor, such as in wear-resistant coatings. Hardness represents how effectively atomic bonds resist localized deformation.

The relatively low hardness values of Ru-based alloys indicate weaker resistance compared to Ni₃Al, meaning that although they remain mechanically stable, they are less suitable for wear-resistant applications. This underscores how bonding strength directly manifests macroscopic hardness and practical material performance limits.

4.5.2.5 Elastic anisotropy

The exploration of elastic anisotropy in crystalline materials offers vital insights into their mechanical properties, particularly in understanding stress distribution under various loading conditions. The elastic response of single crystals typically reflects anisotropic behavior, meaning that the material exhibits different stiffness or deformation characteristics depending on the crystallographic direction of the applied stress.

Elastic anisotropy quantifies how the material's elastic properties, such as Bulk modulus and shear modulus, vary with crystalline orientation. The index proposed by Ranganathan et al. [322] allows for a nuanced description of elastic anisotropy, given as:

$$A^U = (5G_V / G_R) + (B_V / B_R) - 6 \geq 0, \quad (4.20)$$

where $A^U = 0$ indicates isotropic material. The Ranganathan anisotropy criteria is applicable to a wide arrange of material systems, as opposed to the Zener [323] anisotropy index and Chung-Buessem [324] empirical anisotropy index, which are primarily applicable to cubic material systems. In this thesis, the index A^U for cubic and tetragonal crystals are calculated using Ranganathan et al [322], formalism.

Tables 4.9-4.11 presents the elastic anisotropy values for A15-X₃Ru alloys, highlighting significant variations among different compositions. Ni₃Ru exhibits the highest elastic anisotropy value of 33.03, indicating pronounced directional dependence of its elastic properties. In contrast, Co₃Ru shows the lowest elastic anisotropy value of -85.78. In the D0c phase, Cr₃Ru stands out with an elastic anisotropy value of 44.98, representing the highest anisotropic response in this phase. Conversely, Sc₃Ru has the lowest elastic anisotropy of -10.64. In the tP16 phase, Cr₃Ru

again is the demonstrates significant anisotropy, showcasing the lowest elastic anisotropy of -4.80. Ti_3Ru , on the other hand, possesses the highest elastic anisotropy in this phase with a value of 22.53. The order of increasing elastic anisotropy index of compounds in A15 phase are as follows: $\text{Co}_3\text{Ru} < \text{Ti}_3\text{Ru} < \text{Mn}_3\text{Ru} < \text{V}_3\text{Ru} < \text{Sc}_3\text{Ru} < \text{Co}_3\text{Ru} < \text{Zn}_3\text{Ru} < \text{Fe}_3\text{Ru} < \text{Cr}_3\text{Ru} < \text{Ni}_3\text{Ru}$, whilst for D0c phase the increasing elastic anisotropy index: $\text{Sc}_3\text{Ru} < \text{Ti}_3\text{Ru} < \text{Fe}_3\text{Ru} < \text{V}_3\text{Ru} < \text{Ni}_3\text{Ru} < \text{Zn}_3\text{Ru} < \text{Mn}_3\text{Ru} < \text{Co}_3\text{Ru} < \text{Cu}_3\text{Ru} < \text{Cr}_3\text{Ru}$ and for tP16 phase: $\text{Cr}_3\text{Ru} < \text{Fe}_3\text{Ru} < \text{V}_3\text{Ru} < \text{Ni}_3\text{Ru} < \text{Zn}_3\text{Ru} < \text{Mn}_3\text{Ru} < \text{Sc}_3\text{Ru} < \text{Co}_3\text{Ru} < \text{Cu}_3\text{Ru} < \text{Ti}_3\text{Ru}$. Elastic anisotropy reflects how the strength of atomic bonding varies with direction in a crystal. High values indicate a strong directional-dependence of mechanical properties, whereas negative values point to instability. This demonstrates how microscopic bonding geometry and crystal symmetry directly manifest as macroscopic mechanical behavior that depends on direction.

Notably, all examined systems possess anisotropy factors (A^U) deviating from one, underscoring their anisotropic nature. This characteristic renders them susceptible to stress and the formation of micro-cracks under mechanical loading. The observed trends align closely with previous findings reported in the $\text{L1}_2\text{-Ni}_3\text{Al}$ phase [321], suggesting similar underlying mechanisms governing elastic anisotropy across these alloy systems.

4.5.2.6 Melting point temperatures

The melting point of a substance is the temperature at which it changes from a solid to a liquid. This phase change occurs when the vapor pressures of the solid and liquid phases become equal, establishing the specific melting point where both phases coexist in equilibrium. Generally, materials with strong atomic bonding exhibit higher melting points. Consequently, the melting temperature (T_m) serves as a critical indicator of atomic strength in intermetallic compounds, particularly in the context of high-temperature structural applications. Additionally, the melting point is influenced by the free energies of both the liquid and solid phases [325].

For most substances, the melting and freezing points are nearly identical - mercury is a notable example - but some materials, like agar, display distinct temperatures for solid-liquid transitions during heating and cooling. In contrast to boiling points, melting points are largely unaffected by

pressure, as the volume difference between the solid and liquid phases is minimal during the transition [197].

Pure substances typically possess a higher melting point than alloys or impure materials. The presence of impurities lowers the melting point and can widen the temperature range over which melting occurs. Indeed in our previous study on Mo, Mn and Fe doped A15 Cr₃Ru and Ru₃Cr alloys [250], the results showed that Mn and Fe lower the melting temperature of these alloys, whereas Mo doping increases their melting temperature.

While pure metals have a single, distinct melting point, alloys are characterized by a solidus temperature (the point at which melting begins) and a liquidus temperature (the point at which the material is fully molten). Among elements, tungsten boasts the highest melting point at 3683.15 K, while tantalum hafnium carbide (Ta₄HfC₅), a refractory compound, has an even higher melting point of 4488.15 K [197]. Table 4.10 presents a comparison of the melting points of elemental 3d transition metals alongside commonly used binary alloys Ni₃Al and Nb₃Al. In selecting a suitable alloy for high-temperature structural applications, the relationship between melting point temperature and the mechanical properties is crucial. A pioneering study by Fine et.al [326] established an empirical relation between the elastic constants and the melting temperature across a wide range of materials. This research indicated that the melting temperature follows a linear relationship with its elastic constants [326,327], reinforcing the notion that materials with higher melting points typically possess robust mechanical properties.

For cubic compounds, the melting point temperature can be defined as:

$$T_m = 553K + \left(\frac{591K}{Mbar} \right) * C_{11}(Mbar) \pm 300K \quad (4.21)$$

While for D0c and tP16 tetragonal systems, the melting point temperature is given as:

$$T_m = 354K + \left(\frac{450K}{Mbar} \right) * \left[\frac{1}{3} (2C_{11} + C_{33}(Mbar) \pm 300K) \right] \quad (4.22)$$

Table 4.12: Melting temperatures (K) for elemental 3d-transition metals and commonly used alloys for high-temperature structural applications provided for reference.

3d-transition metals and commonly used binary alloys	Melting temperatures (T_m) ^{Exp}
Sc	1814 K [328]
Ti	1943 K [328]
V	2190 K [328]
Cr	2133 K [328]
Mn	1517 K [328]
Fe	1422 K [328]
Co	1768 K [328]
Ni	1726 K [328]
Cu	1357 K [328]
Zn	692 K [328]
Ru	2607 K [197]
Ni ₃ Al	1691 K [53,197]
Nb ₃ Al	2333 K [329]

where C_{ij} represents the elastic constants of the material. These relations imply that changes in the elastic constants directly influence the melting temperature of alloys, underscoring the significance of these parameters in the design and selection of materials for demanding engineering applications. Equation (4.22) is also applicable to hexagonal and tetragonal intermetallic. However, elemental metals in groups 3b and 4b, along with the lanthanides and actinides, deviate from this correlation.

Tables 4.9-4.11 present the calculated melting temperatures of the various X_3Ru alloys in the A15, D0c and tP16 X_3Ru phases. A comparative analysis of the melting temperature across the three phases is illustrated in Figure 4.8 while Figure 4.9 illustrates trends across the 3d series. In the A15 phase, the melting temperatures range from 1013.98 K (Sc₃Ru) to 7295.48 K (Fe₃Ru) with Fe₃Ru having the highest melting temperature. The calculated melting temperatures (T_m) for Fe₃Ru (7295.48 K), Ti₃Ru (6823.51 K), V₃Ru (1983.22 K), Cr₃Ru (2538.76 K), and Co₃Ru (5074.15 K) compare favorably or exceed those of the widely alloys like Ni₃Al (1691 K) [53] and Nb₃Al (2333 K) [330]. The order of increasing melting temperature in A15 phase is as follows: Sc₃Ru < Zn₃Ru < Ni₃Ru < Mn₃Ru < Cu₃Ru < V₃Ru < Cr₃Ru < Co₃Ru < Ti₃Ru < Fe₃Ru. In the D0c phase, the

melting temperatures range from 732.18 K (Sc_3Ru) to 1821.44 K (Fe_3Ru) with Fe_3Ru having the highest melting temperature. The calculated T_m values for Fe_3Ru (1821.44 K), Co_3Ru (1717.64 K), and Ni_3Ru (1756.23 K) meet or surpass these benchmarks. In the tP16 phase, the melting temperature ranged from 516.68 K (Cr_3Ru) to 1795.19 K (Ni_3Ru) with Ni_3Ru having the highest melting temperature. Fe_3Ru (1794.87 K) and Ni_3Ru (1795.19 K) exhibit comparable or higher T_m values than Ni_3Al and Nb_3Al . The order of increasing melting temperature in tP16 phase is as follows: $\text{Cr}_3\text{Ru} < \text{Sc}_3\text{Ru} < \text{Ti}_3\text{Ru} < \text{Mn}_3\text{Ru} < \text{V}_3\text{Ru} < \text{Zn}_3\text{Ru} < \text{Cu}_3\text{Ru} < \text{Co}_3\text{Ru} < \text{Fe}_3\text{Ru} < \text{Ni}_3\text{Ru}$. A clear trend in the melting temperature is observed from Mn_3Ru to Zn_3Ru across both the D0c and tP16 phases. Melting temperature is a direct indicator of atomic bond strength and lattice stability. Alloys with very high T_m , such as Fe_3Ru and Ni_3Ru , possess exceptionally strong interatomic forces, making them thermally robust compared to benchmark alloys like Ni_3Al . In contrast, lower T_m values in alloys such as Sc_3Ru or Cr_3Ru reflect weaker bonding. This highlights how bond energies and crystal symmetry give rise to macroscopic thermal stability. Among all the studied phases, Fe_3Ru stands out with the highest melting temperature as shown in figure 4.9. However, for these identified alloys to be deemed suitable for high-temperature structural applications, additional factors such as thermodynamic stability and mechanical stability, as discussed in Sections 4.2 and 4.5, must be considered. A summary of these parameters for each alloy is provided below.

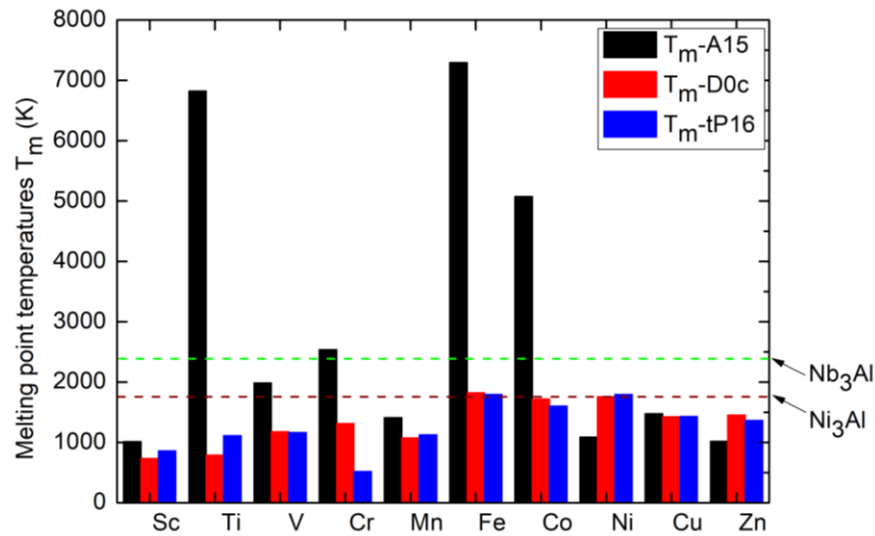


Figure 4.8: Calculated melting temperatures (T_m) of (a) A15, (b) D0c and (c) tP16 X_3Ru structures. The brown dotted line represents Ni_3Al (1691 K) whilst the green dotted line represents Nb_3Al (2333 K).

4.5.2.6.1 A15 Ti₃Ru

The calculated value of the heat of formation for A15 Ti₃Ru alloy is 0.88 eV/atom, indicating thermodynamic instability under equilibrium conditions. However, as addressed in section 4.2, stability can be achieved through non-equilibrium techniques or via doping. Alongside its high-melting temperature (6823.51 K), A15 Ti₃Ru possesses remarkable properties, including a high ductility (7.0), a high bulk modulus (403 GPa), and a low density (6.01 g/cm³) as discussed in the preceding sections. These characteristics render the alloy a strong candidate for high-temperature applications, as it can endure significant plastic deformation before fracture. Its high ductility allows it to withstand considerable loads and stress without failing, thereby enhancing its reliability in extreme conditions. Furthermore, the alloy's excellent compression resistance, combined with its lightweight nature, positions it as an ideal candidate for applications that demand both strength and reduced mass.

4.5.2.6.3 A15 Cr₃Ru

In contrast, the calculated heat of formation for the A15 Cr₃Ru alloy is -0.49 eV/atom, indicating that the system is thermodynamically stable under equilibrium conditions, thus making experimental synthesis feasible. In addition to its high melting temperature (2538.76 K), Cr₃Ru boasts high ductility (19.6), a high bulk modulus (275 GPa), low density (4.88 g/cm³), and excellent mechanical stability ($C_{ij} > 0$).

These properties make this alloy particularly suitable for high-temperature environments, as it can endure significant plastic deformation before fracture and resist structural failure. Its high ductility allows it to undergo significant plastic deformation without breaking, contributing to its excellent performance characteristics. Furthermore, the alloy's exceptional compressive resistance coupled with its low-density positions as an ideal candidate for lightweight, high-strength applications.

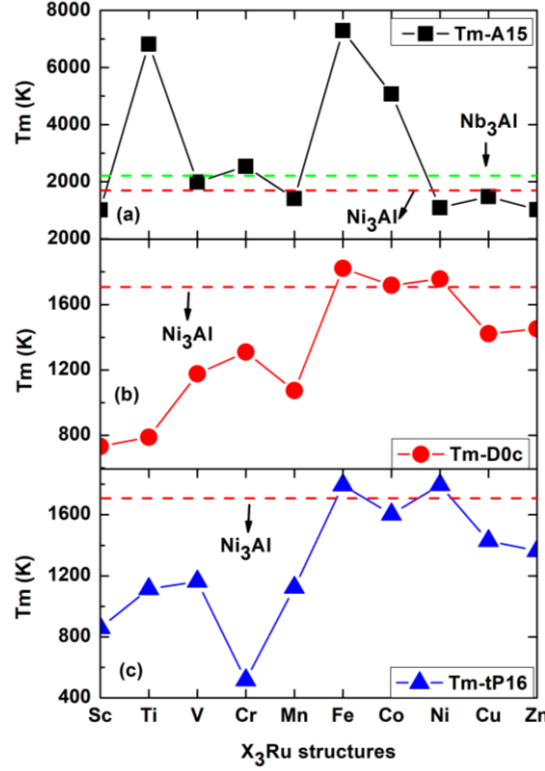


Figure 4.9: Calculated trends in melting temperatures (T_m) of (a) A15, (b) D0c and (c) tP16 X_3Ru structures. The red dotted line represents Ni_3Al (1691 K) whilst the green dotted line represents Nb_3Al (2333 K).

Reducing the weight of turbine rotating components is crucial for decreasing engine energy consumption and minimizing greenhouse gas emissions, further underscoring the significance of the Cr_3Ru alloy in advanced engineering applications.

4.5.2.6.4 A15 and D0c Co_3Ru

The calculated heat of formation values for A15 and D0c Co_3Ru alloy are 1.41 eV/atom and 0.10 eV/atom, respectively, indicating that these systems are thermodynamically unstable under equilibrium conditions. Beyond their elevated melting temperatures (5074.15 K and 1717.64 K respectively) both alloys exhibit remarkable physical and magnetic properties. The A15 Co_3Ru boasts a high bulk modulus (335 GPa) and magnetic moment ($1.70 \mu_B$), while the D0c Co_3Ru alloy features a bulk modulus of 200 GPa, excellent mechanical stability ($C_{ij} > 0$), and a magnetic moment ($1.82 \mu_B$) comparable to the widely used $L1_2-Ni_3Al$ alloy. These characteristics make both

alloys highly suitable for high-temperature environments, as they provide outstanding resistance to compression and structural failure under applied loads. Furthermore, their magnetic properties broaden their applicability in fields such as electronics, telecommunications, energy production, and medical imaging.

4.5.2.6.5 D0c Fe₃Ru and tP16 Fe₃Ru

The calculated heat of formation values for the D0c Fe₃Ru and tP16 Fe₃Ru alloys are 0.11 eV/atom and 0.07 eV/atom, respectively, indicating that these alloys are thermodynamically unstable under equilibrium conditions. However, they can be stabilized under non-equilibrium conditions. Both alloys are characterized by high melting temperatures (1821.44 K and 1794.87 K respectively) and exhibit unique magnetic and mechanical properties. Notably, D0c Fe₃Ru possesses a magnetic moment of 2.52 μ_B , while tP16 Fe₃Ru features a high bulk modulus (186 GPa), ductility (2.6), and a magnetic moment of 0.95 μ_B , surpassing the commonly used L1₂-Ni₃Al alloy. These properties make both alloys well-suited for high-temperature environments, with tP16 Fe₃Ru offering exceptional compression resistance for high-strength applications. Furthermore, their magnetic properties make them ideal for use in electronics, telecommunications, energy production, and medical imaging.

Chapter Five

Pressure dependent structural stability, electronic and mechanical stability of X_3Ru ($X = Cr, Mn$) in A15, D0c and tP16 crystallographic phases

To date, the influence of pressure on the properties of transition metal – Ru based alloys has not been investigated, either theoretically or experimentally. External parameters such as temperature, pressure, strain, and electric or magnetic fields can profoundly alter material properties. Among these, pressure is a critical thermodynamic variable that modifies properties by reshaping microscopic structures, interatomic electrostatic interactions, electronic orbitals, and chemical bonding [331–335]. Over the past decades, pressure has proven to be a powerful tool for discovering materials that remain unattainable under standard conditions. [336–346].

While significant experimental and limited theoretical work has been devoted to Ru-based alloys, there remains a lack of systematic investigations into pressure dependent structural, electronic, mechanical, and magnetic properties. This gap is critical, as understanding these properties is essential for advancing the design of alloys capable of withstanding extreme environments. In Chapter Four, we demonstrated that Mn_3Ru in the A15, D0c, and tP16 phases is thermodynamically and mechanically stable, metallic, and exhibits strong magnetism compared to all other X_3Ru ($X = Sc-Zn$) systems. Importantly, Mn_3Ru can be synthesized experimentally, positioning it as a promising candidate for high-temperature applications. In addition, Mn_3Ru shows potential for high-temperature structural applications due to its superior stability and magnetism.

In this section, we advance our analysis by presenting the structural, electronic, and elastic properties of Mn_3Ru and Cr_3Ru in the A15, D0c, and tP16 phases under applied pressure, using the practical hypothesis established in Chapter Three. While Mn_3Ru has been demonstrated to exhibit potential for high-temperature structural applications due to its superior stability and magnetism, Cr_3Ru has already been synthesized experimentally. By systematically examining the behavior of Mn_3Ru and Cr_3Ru under pressure, we aim to uncover the underlying mechanisms and

properties of these materials under varying external pressure conditions. Specifically, the structural, electronic, and mechanical properties of Mn_3Ru and Cr_3Ru are examined, by applying incremental hydrostatic pressures of 1, 5, 10, 15, 20, 50, 100, 150, 200, 250, and 300 GPa simultaneously along the x, y, and z directions within the respective crystal systems, in addition to the computational details outlined in Chapter 4.

Pressure, as a thermodynamic variable, can significantly alter microscopic structures, interatomic interactions, and bonding characteristics, thereby offering a pathway to tune alloy properties. The outcomes of this study do not only provide a deeper understanding of how Ru-based alloys respond to external stimuli but also establish design principles for tailoring their performance.

5.1 Brief literature on related alloys under pressure

Recent studies have increasingly focused on the structural, electronic, and mechanical properties of various intermetallic alloys under pressure. For instance, Chen et al. [347] investigated the thermodynamic, elastic and electronic properties of Al_3V and Al_3Nb intermetallic alloys using DFT techniques, revealing that pressure enhances their elastic constants, bulk, shear, and Young's modulus. Similarly, Durukan's [348] studied the mechanical, vibration and optical properties of IrAl intermetallic compound in the B2 phase and demonstrated that pressure reduces the lattice parameter while increasing their elastic constants and maintaining mechanical stability. These findings align with previous research on Ni_3X ($\text{X} = \text{Al}, \text{Ga}$ and Ge) and Pt_3Al alloys by Chen et al. [347] and Liu et al. [349] respectively, which also highlighted the significance of pressure in altering the properties of intermetallic alloys. To date, systematic studies on the structural, electronic, mechanical, and magnetic properties of the proposed Ru-based alloys under pressure remain limited literature. This gap highlights the need for further investigation in this area.

5.2 Structural stability of Cr_3Ru and Mn_3Ru under pressure

The calculated lattice constants, volumes, heats of formation, magnetic moments, densities, and bond lengths of the A15, D0c, and tP16 Cr_3Ru and Mn_3Ru alloys under varying pressure conditions are presented in Tables 5.1-5.6. A trend of decreasing lattice constants with decreasing bond-length

and increasing density under applied pressures from 1 GPa to 300 GPa across the D0c and tP16 phases is observed, which reflects how external pressure modifies interatomic interactions. Applying pressure forces atoms closer together, which increases electron cloud overlapping and strengthens short-range repulsive interactions. To balance these repulsive forces with the attractive bonding interactions, the system minimizes its free energy by contracting the lattice, leading to shorter bond-lengths and reduced lattice constants. The simultaneous increase in density is a direct consequence of this compression, as the same number of atoms occupy a smaller volume. The clear correlation observed between lattice constants, bond-length, and density from 10 GPa to 300 GPa across A15 phase highlights the regime where compression dominates the interatomic balance, driving the alloys toward more compact and energetically favorable configurations. In essence, pressure induces a restructuring of atomic spacing and electronic interactions, which drives the system toward denser atomic packing and directly influences the stability of different phases. At zero pressure, the calculated heat of formation for Mn_3Ru in the A15 phase is negative (-0.64 eV/atom), which signifies that the alloy is thermodynamically stable under equilibrium conditions and can be synthesized through conventional equilibrium methods such as slow cooling or annealing.

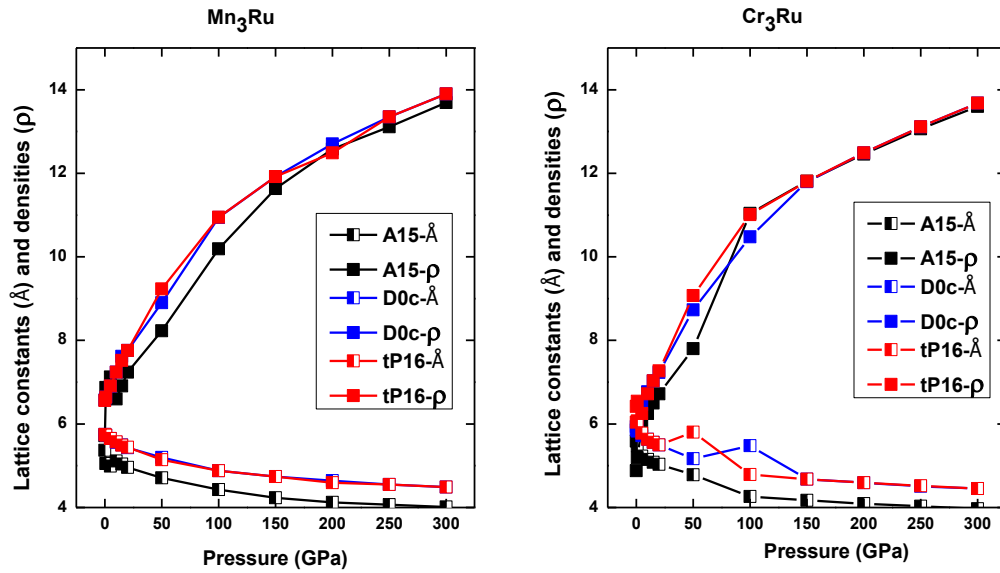


Figure 5.1: The calculated lattice constants and density of A15, D0c and tP16 X_3Ru ($\text{X} = \text{Cr}$ and Mn) at different pressures. The half-square graphs represent the lattice constants, and the full-squares graphs are for density respectively.

In contrast, A15 Cr₃Ru exhibits a positive heat of formation (0.22 eV/atom), as shown in Table 5.1 and 5.2 indicating thermodynamic instability under equilibrium conditions; however, this does not preclude its formation, as metastable phases can be realized through non-equilibrium synthesis routes such as rapid quenching, ion implantation, or thin-film deposition. When pressure is applied, A15 Mn₃Ru undergoes a transition from stability to instability, as its heat of formation shifts from negative to increasingly positive values, reflecting the destabilizing effect of compression on Mn–Ru bonding interactions. For A15 Cr₃Ru, pressure further increases the already positive heat of formation, amplifying its instability. Therefore, pressure modifies the electronic and bonding environment in these alloys, reducing their energetic favorability. This means A15 Mn₃Ru is best synthesized at ambient conditions, while A15 Cr₃Ru requires kinetic control via non-equilibrium techniques, and high-pressure synthesis is generally unfavorable for stabilizing alloy in the A15 phase.

In the D0c phase, Mn₃Ru shows a strongly negative heat of formation (–1.61 eV/atom) at zero pressure, confirming its thermodynamic stability under equilibrium conditions, while D0c Cr₃Ru has a slightly positive heat of formation (0.13 eV/atom), as shown in Table 5.3 and 5.4 indicating instability at ambient conditions. When pressure is applied, D0c Mn₃Ru remains stable but its stability gradually decreases, reflecting the weakening of Mn–Ru bonding interactions under compression. In contrast, Cr₃Ru undergoes a notable transformation: although unstable at zero pressure, it becomes thermodynamically stable at higher pressures, with negative heats of formation observed at 20 GPa (–0.85 eV/atom), 50 GPa (–0.27 eV/atom), and 100 GPa (–0.29 eV/atom). This behavior highlights the pressure-induced stabilization, where compression modifies electronic structure and atomic bonding, favoring alloy formation in Cr–Ru that is otherwise unfavorable at ambient conditions. Therefore, D0c Mn₃Ru can be synthesized under equilibrium conditions at ambient pressure, but its stability diminishes under high pressure, making compression less suitable for synthesis. D0c Cr₃Ru, however, requires non-equilibrium methods at ambient conditions but becomes accessible to equilibrium synthesis at sufficiently high pressures, where pressure stabilizes the alloy in the D0c phase. Thus, pressure acts as a tuning parameter: destabilizing Mn₃Ru while enabling the stabilization and equilibrium synthesis of Cr₃Ru.

Table 5.4: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of A15, Mn₃Ru at different pressures.

Pressure (GPa) A15 Mn ₃ Ru (a)	Lattice constants (Å)	Heat of formation (eV/atom)	Magnetic Moment (μ _B /atom)	Density $\rho = g / cm^3$	Bond length of Mn-Ru (Å)
0	5.37	-0.64	3.88	5.72	2.999
1.0	5.05	0.95	1.16	6.87	2.822
5	4.99	1.23	1.14	7.12	2.788
10	5.11	1.22	0.56	6.60	2.859
15	5.04	0.84	0.53	6.91	2.816
20	4.96	0.87	2.58	7.24	2.772
50	4.71	0.92	2.40	8.23	2.635
100	4.43	0.89	0.49	10.19	2.474
150	4.23	1.24	0.49	11.63	2.367
200	4.12	1.62	1.03	12.58	2.306
250	4.07	1.51	0.93	13.11	2.300
300	4.01	1.60	1.01	13.69	2.296

Table 5.2: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of A15, Cr₃Ru at different pressures.

A15 Cr ₃ Ru GPa	Lattice constants (Å)	Heat of formation (eV/atom)	Magnetic Moment (μ _B /atom)	Density $\rho = g / cm^3$	Bond length of Cr-Ru (Å)
0	5.59	0.22	4.19	4.88	3.126
1.0	5.48	0.81	0.96	5.19	3.063
5	5.23	1.13	3.26	5.95	2.926
10	5.15	1.12	3.23	6.25	2.879
15	5.08	1.11	3.21	6.50	2.841
20	5.03	1.09	3.19	6.72	2.811
50	4.78	0.72	3.08	7.80	2.674
100	4.26	1.62	0.00	11.04	2.382
150	4.17	1.60	0.13	11.81	2.329
200	4.09	1.63	0.01	12.46	2.287
250	4.03	1.61	0.00	13.06	2.252
300	3.97	1.61	0.00	13.60	2.222

Table 5.3: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of D0c, Mn₃Ru structure at different pressures.

Mn ₃ Ru Pressure (GPa)	Lattice constants a = (Å)	Heat of formation (eV/atom)	Magnetic Moment (μ_B /atom)	Density $\rho = g / cm^3$	Bond length of Mn-Ru (Å)
0	5.75	-1.61	3.25	6.57	2.876
1.0	5.73	-0.11	3.24	6.64	2.863
5	5.65	-0.04	3.22	6.90	2.826
10	5.56	-0.04	3.21	7.24	2.782
15	5.50	-0.04	3.21	7.62	2.749
20	5.43	-0.05	3.19	7.76	2.716
50	5.20	-0.06	2.95	8.90	2.602
100	4.88	-0.48	0.40	10.94	2.439
150	4.74	-0.31	0.26	11.92	2.372
200	4.64	-0.19	0.19	12.70	2.320
250	4.55	-0.12	0.15	13.35	2.277
300	4.49	-0.06	0.10	13.90	2.244

Table 5.4: The calculated lattice constants, heat of formation, magnetic moment, density, and bond-length of D0c, Cr₃Ru at different pressures.

Cr ₃ Ru P (GPa)	Lattice constants a = (Å)	Heat of formation (eV/atom)	Magnetic Moment (μ_B /atom)	Density $\rho = g / cm^3$	Bond length of Cr-Ru (Å)
0	5.86	0.13	2.97	5.94	2.945
1.0	5.83	0.13	2.96	6.01	2.913
5	5.72	0.13	2.96	6.46	2.858
10	5.63	0.11	2.95	6.77	2.816
15	5.56	0.10	2.94	7.03	2.779
20	5.50	-0.85	2.93	7.23	2.749
50	5.17	-0.27	2.40	8.73	2.586
100	5.48	-0.29	0.52	10.48	2.741
150	4.68	0.28	0.00	11.80	2.338
200	4.59	0.30	0.00	12.49	2.296
250	4.51	0.33	0.00	13.11	2.257
300	4.45	0.36	0.00	13.68	2.224

In the tP16 phase, Mn₃Ru exhibits a strongly negative heat of formation (−1.61 eV/atom) at zero pressure, confirming its thermodynamic stability under equilibrium conditions, while tP16 Cr₃Ru shows a slightly positive heat of formation (0.11 eV/atom), as shown in Table 5.5 and 5.6

indicating instability at ambient conditions. Under pressure, tP16 Mn₃Ru remains stable but its stability gradually decreases, reflecting the weakening of Mn–Ru bonding interactions as compression alters atomic distances and electronic overlap. In contrast, tP16 Cr₃Ru undergoes a significant transformation: although unstable at zero pressure, it becomes thermodynamically stable at specific pressures, with negative heats of formation observed at 1 GPa (–0.17 eV/atom), 20 GPa (–0.85 eV/atom), and 50 GPa (–0.74 eV/atom). This pressure-induced stabilization highlights the electronic structure modification under compression, where bonding interactions that are unfavorable at ambient conditions become energetically favorable at certain pressure ranges. This implies that Mn₃Ru can be synthesized under equilibrium conditions at ambient pressure, but its stability diminishes under high compression, making pressure less advantageous for synthesis.

Table 5.5: The calculated lattice constants, heat of formation, magnetic moment, density and bond-length of tP16, Mn₃Ru at different pressures.

System Mn ₃ Ru tP16 Pressure (GPa)	Lattice constants a = (Å)	Heat of formation (eV/atom)	Magnetic Moment (μ _B /atom)	Density $\rho = g / cm^3$	Bond length of Mn-Ru (Å)
0	5.75	-1.61	3.25	6.56	2.874
1.0	5.73	-0.11	3.24	6.64	2.856
5	5.65	-0.04	3.22	6.91	2.827
10	5.57	-0.04	3.21	7.24	2.784
15	5.49	-0.04	3.21	7.52	2.747
20	5.44	-0.05	3.18	7.76	2.718
50	5.14	-0.26	0.93	9.23	2.569
100	4.88	-0.47	0.39	10.95	2.438
150	4.74	-0.31	0.26	11.92	2.371
200	4.59	-0.19	0.19	12.49	2.296
250	4.55	-0.12	0.14	13.35	2.277
300	4.49	-0.06	0.10	13.90	2.243

Table 5.6: The calculated lattice constants, heat of formation, magnetic moment, density and bond-length of tP16, Cr₃Ru at different pressures.

System Cr ₃ Ru tP16	Lattice constants (a = Å)	Heat of formation (eV/atom)	Magnetic Moment (μ_B /atom)	Density $\rho = g / cm^3$	Bond length of Cr-Ru (Å)
0	6.04	0.11	0.68	6.42	3.022
1.0	6.07	-0.17	0.69	6.54	3.034
5	5.78	0.10	2.92	6.25	2.890
10	5.63	0.11	2.94	6.72	2.814
15	5.56	0.10	3.92	7.03	2.779
20	5.50	-0.85	2.93	7.27	2.749
50	5.80	-0.74	0.60	9.07	2.900
100	4.79	0.26	0.00	11.01	2.394
150	4.68	0.28	0.00	11.81	2.338
200	4.59	0.30	0.00	12.49	2.296
250	4.52	0.33	0.00	13.11	2.259
300	4.45	0.36	0.00	13.68	2.225

tP16 Cr₃Ru, however, which is metastable at ambient conditions, becomes accessible to equilibrium synthesis at selected high-pressure ranges where stability is enhanced. Thus, pressure acts as a critical tuning parameter: reducing the stability of Mn₃Ru while enabling the stabilization and equilibrium synthesis of Cr₃Ru in the tP16 phase. Comparing the formation energies of the A15, D0c, and tP16 phases for Mn₃Ru and Cr₃Ru alloys (Figure 5.1) reveal clear trends in their relative thermodynamic stability. At zero pressure, Mn₃Ru consistently shows negative heats of formation across all phases (A15: -0.64 eV/atom, D0c: -1.61 eV/atom, tP16: -1.61 eV/atom), confirming that it is thermodynamically stable under equilibrium conditions. Among these, the D0c and tP16 phases are the most stable, with significantly lower formation energies compared to the A15 phase, suggesting that Mn₃Ru favors these structures energetically. Cr₃Ru, on the other hand, exhibits positive heats of formation at zero pressure in all phases (A15: +0.22 eV/atom, D0c: +0.13 eV/atom, tP16: +0.11 eV/atom), indicating thermodynamic instability under ambient equilibrium conditions. However, under applied pressure, Cr₃Ru shows pressure-induced stabilization: in the D0c phase, stability emerges at 20–100 GPa, while in the tP16 phase, stability is achieved at relatively lower pressures (1 GPa, 20 GPa, and 50 GPa). This demonstrates that

pressure modifies the electronic structure and bonding interactions in Cr–Ru, enabling phases that are unstable at ambient conditions to become energetically favorable.

5.2.1 Induced magnetic moments

The magnetic moment trends in Mn_3Ru and Cr_3Ru alloys in the A15 phase reflect how pressure modifies the electronic structure and spin polarization of the system. At zero pressure, Mn_3Ru has a relatively large magnetic moment ($3.88 \mu_B$), while Cr_3Ru shows a smaller but finite moment ($0.68 \mu_B$), as shown in Table 5.1, 5.2 and Figure 5.2 both indicating magnetic behavior. Under compression, Mn_3Ru 's magnetic moment decreases steadily, which can be understood as pressure enhancing orbital overlap and bandwidth, thereby delocalizing electrons and reducing spin polarization.

In A15 Cr_3Ru , however, magnetization is initially enhanced at low to moderate pressures (1–20 GPa), suggesting that compression improves exchange interactions and stabilizes spin alignment in this regime. At very high pressures (100–300 GPa), Cr_3Ru loses its magnetization completely, reflecting a transition to a non-magnetic state as electron delocalization dominates and exchange splitting collapses.

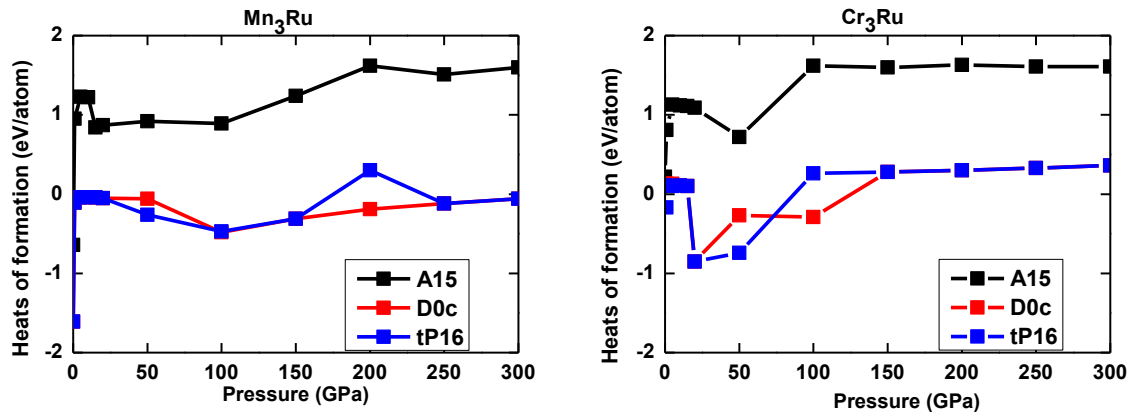


Figure 5.2: Calculated heat of formation as a function of pressure for A15, D0c and tP16 X_3Ru ($\text{X} = \text{Cr}$ and Mn) under pressure.

In the D0c phase, Mn_3Ru and Cr_3Ru both exhibit magnetic behavior at zero pressure, with magnetic moments of $3.25 \mu_B$ and $2.97 \mu_B$ respectively. Under compression, D0c Mn_3Ru retains its magnetization up to moderate pressures, but from 100 GPa to 300 GPa its magnetic moment decreases sharply, reflecting the pressure-induced delocalization of electrons and the weakening of exchange interactions that sustain magnetism (as shown in Figure 5.1). D0c Cr_3Ru , on the other hand, maintains magnetization across lower and intermediate pressures (1–100 GPa), suggesting that compression initially enhances exchange coupling and stabilizes spin alignment. However, at very high pressures (150–300 GPa), Cr_3Ru loses its magnetization completely, indicating a collapse of spin polarization as band broadening dominates and the exchange splitting vanishes.

In the tP16 phase, Mn_3Ru and Cr_3Ru both exhibit magnetic behavior at zero pressure, with magnetic moments of $3.25 \mu_B$ and $0.68 \mu_B$ respectively. Under compression, Mn_3Ru retains its magnetization up to moderate pressures but begins to decrease sharply from 50 GPa to 300 GPa. This trend reflects the pressure-induced band broadening: as atoms are forced closer together, electron orbitals overlap more strongly, leading to delocalization of electrons and a reduction in exchange splitting, which weakens spin polarization and suppresses magnetism.

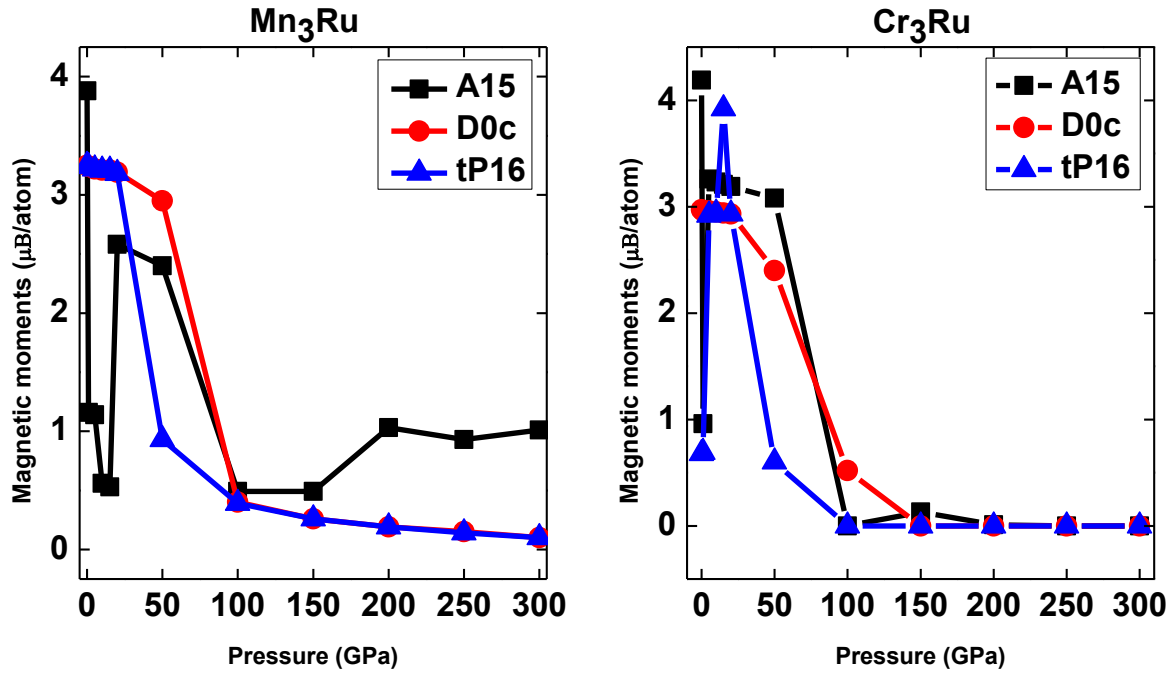


Figure 5.5: Calculated magnetic moments as a function of pressure for A15, D0c and tP16 X_3Ru ($\text{X} = \text{Cr}$ and Mn) under pressure.

Cr₃Ru, on the other hand, shows an initial increase in magnetization at low pressures (1–20 GPa), suggesting that moderate compression enhances exchange interactions and stabilizes spin alignment. However, at 50 GPa the magnetization begins to decrease, and from 100 GPa to 300 GPa it vanishes completely, indicating a collapse of magnetic order as pressure overwhelms exchange interactions and drives the system into a non-magnetic state (Figure 5.3). When comparing the magnetic moment trends of Mn₃Ru and Cr₃Ru across the A15, D0c, and tP16 phases, several clear observations emerge. At zero pressure, Mn₃Ru consistently exhibits higher magnetic moments (A15: 3.88 μ_B , D0c: 3.25 μ_B , tP16: 3.25 μ_B) compared to Cr₃Ru (A15: 0.68 μ_B , D0c: 2.97 μ_B , tP16: 0.68 μ_B), indicating that Mn₃Ru is intrinsically more magnetic and most thermodynamically stable across phases. Among the phases, the A15 Mn₃Ru shows the strongest magnetization at ambient conditions, while Cr₃Ru displays phase-dependent magnetism, with relatively higher values in the D0c phase but weaker in A15 and tP16. Under pressure, Mn₃Ru generally retains magnetization but experiences a gradual suppression at higher pressures (especially beyond 50–100 GPa), reflecting pressure-induced electron delocalization and reduced exchange splitting. Cr₃Ru, by contrast, shows a tunable response: magnetization is enhanced at low to moderate pressures in some phases (A15 and tP16), maintained in D0c up to ~100 GPa, but collapses completely at very high pressures (150–300 GPa), indicating a transition to a non-magnetic state.

5.2.2 Density

From Table 5.1- 5.6, Analyzing the pressure dependent densities of Mn₃Ru and Cr₃Ru across the three phases (A15, D0c, and tP16) reveals clear differences in structural compactness and implications for lightweight applications.

- A15 phase: Mn₃Ru (5.72 g/cm³) and Cr₃Ru (4.88 g/cm³) both have lower densities compared to Ni₃Al (6.14 g/cm³), suggesting potential for lightweight applications at ambient pressure. Cr₃Ru in A15 is the lightest among all cases.
- D0c phase: Mn₃Ru (6.57 g/cm³) and Cr₃Ru (5.94 g/cm³) show higher densities than in A15, with Mn₃Ru exceeding Ni₃Al. This indicates that D0c Mn₃Ru is relatively heavy and less suitable for lightweight design, while Cr₃Ru remains lighter but denser than its A15 counterpart.

- tP16 phase: Mn_3Ru (6.56 g/cm^3) and Cr_3Ru (6.42 g/cm^3) both approach or exceed Ni_3Al 's density, meaning these phases are not advantageous for lightweight applications. However, under applied pressure, the densities of Mn_3Ru and Cr_3Ru alloys increase significantly (as shown in Figure 5.1).

These results are due to pressure-induced lattice contraction: as external pressure forces atoms closer together, bond lengths decrease, lattice constants shrink, and the same number of atoms occupy a smaller volume, thereby increasing density. This densification reflects the balance between repulsive and attractive interatomic forces being shifted toward more compact atomic packing under compression. In summary, Cr_3Ru (A15) is the lightest phase and the best candidate for lightweight applications, but its thermodynamic instability at zero pressure poses a challenge for synthesis. Mn_3Ru is more stable but heavier, limiting its lightweight potential.

5.3 Electronic and magnetic properties

Electronic and magnetic properties under pressure are important because they reveal how atomic spacing and electron behavior respond to external stress. Pressure alters orbital overlap and band structure, often leading to band broadening, changes in conductivity, or even metal–insulator transitions. At the same time, magnetism driven by spin polarization and exchange interactions can be enhanced at moderate compression or suppressed entirely at very high pressures as electrons become more delocalized. These pressure-dependent changes provide insight into phase stability, guide synthesis strategies, and enable the design of materials with tunable functionalities, such as switchable conductivity or controllable magnetism, which are valuable for advanced structural, electronic, and spintronic applications. This section examines the electronic and magnetic properties of the most stable Mn_3Ru and Cr_3Ru alloys in the A15, D0c, and tP16 phases under pressure through an analysis of the density of states. To ensure accurate and reliable density of states plots, in addition to the computational parameters outlined in Section 4.1 will also be used in this section,

5.3.1 Spin polarization and magnetization

Figures 4-9 present the spin-polarized total density of states (DOS) for $X_3\text{Ru}$ ($X = \text{Cr}, \text{Mn}$) alloys across the A15, D0c, and tP16 phases, respectively. In the D0c and tP16 phases of Mn_3Ru , the TDOS at low pressures (0–50 GPa) shows asymmetry between spin-up and spin-down bands, with the Fermi level intersecting only one spin channel. This indicates nearly 100% spin polarization at Fermi energy, a hallmark of half-metallic behavior. In the A15 phase, Mn_3Ru also exhibits asymmetric bands at both low and high pressures, maintaining strong spin polarization. For Cr_3Ru , the D0c phase displays similar asymmetry at low pressures (0–100 GPa), while in the tP16 and A15 phases, asymmetry is observed within the 0–50 GPa range, again suggesting nearly full spin polarization.

In the Mn_3Ru D0c phase, the TDOS profiles from 100–300 GPa show symmetric spin-up and spin-down bands, while in the tP16 phase this symmetric behavior emerges from 150–300 GPa. Such symmetry between spin channels eliminates the imbalance that drives magnetization, leading to cancellation of the net magnetic moment associated with electronic spin. This explains the zero magnetic moments calculated in these systems (Tables 5.1–5.6). In conclusion, alloys that exhibit asymmetric spin-up and spin-down bands possess the highest magnetic moments because the imbalance at the Fermi level drives strong spin polarization. This pronounced spin asymmetry translates into robust magnetic properties, making such systems highly attractive for spintronic applications, particularly as spin filters and spin injection materials where nearly 100% spin-polarized currents are required.

5.3.2 Metallic characteristics and conductivity

In the A15 phase, the TDOS analysis shows that Mn_3Ru is half-metallic at zero pressure, with the Fermi level crossing bands in only one spin channel while the other remains semiconducting. Under pressure, additional states appear at the Fermi level, driving a transition from half-metallic to metallic behavior, except at 20 GPa and 50 GPa where half-metallicity persists. The decrease in states between -0.5 eV and 0 at 100–300 GPa compared to 1–50 GPa reflects pressure-induced band broadening and electron delocalization, which weakens spin polarization. In Cr_3Ru , the

TDOS indicates metallic character at zero pressure, with pressure further enhancing metallic conductivity due to stronger overlap of valence and conduction bands at the Fermi level. At high pressures (100–300 GPa), the reduction of states in the valence region and increase in the conduction region highlight the redistribution of electronic states, consistent with pressure-driven band restructuring.

In the D0c phase, the TDOS plots for Mn_3Ru alloys at zero and varying pressures reveal a strong overlap between valence and conduction bands at the Fermi level, producing a high density of states that underpins metallic conductivity. This behavior is consistent with the metallic character observed in A15 Mn_3Ru and Cr_3Ru (except at 0, 20, and 50 GPa), where band overlap ensures charge carriers are readily available. The observed reduction of states in the valence region (–0.5 eV to 0 eV) at high pressures (100–300 GPa) compared to lower pressures (0–50 GPa) reflects pressure-induced band broadening and electron redistribution.

In the tP16 phase, the TDOS profiles for Mn_3Ru at zero and varying pressures show a pronounced overlap between valence and conduction bands at the Fermi level, confirming metallic behavior and enhanced conductivity similar to the D0c phase. The reduction of states in the valence region (–0.5 eV to 0 eV) at high pressures (100–300 GPa) compared to lower pressures (0–50 GPa) reflects pressure-induced band broadening and electron redistribution. For Cr_3Ru , the TDOS indicates half-metallicity at zero pressure, with the Fermi level crossing bands in only one spin channel. Under pressure, the states at the Fermi level increase up to 20 GPa, enhancing conductivity, revert to half-metallicity at 50 GPa, and then transition to full metallic behavior from 100–300 GPa. The reduction of states in the valence region (–0.5 eV to 0 eV) at high pressures (100–300 GPa) for both compounds compared to lower pressures (0–50 GPa) reflects pressure-induced band broadening and electron redistribution.

Across the A15, D0c, and tP16 phases, Mn_3Ru and Cr_3Ru exhibit distinct TDOS behaviors that highlight the influence of crystal structure and pressure on electronic properties. In the A15 phase, Mn_3Ru is half-metallic at zero pressure but transitions to metallic under compression, while Cr_3Ru is metallic throughout, with conductivity enhanced by increasing states at the Fermi level. In the D0c phase, both Mn_3Ru and Cr_3Ru display strong metallic character at all pressures due to

pronounced overlap of valence and conduction bands, though high pressures redistribute states and reduce valence contributions. In the tP16 phase, Mn_3Ru remains metallic across all pressures, with conductivity strengthened by compression, whereas Cr_3Ru is half-metallic at zero pressure, becomes more conductive up to 20 GPa, reverts to half-metallicity at 50 GPa, and finally transitions to metallic behavior at 100–300 GPa. Overall, Mn_3Ru demonstrates robust metallic conduction with limited half-metallicity, while Cr_3Ru shows tunable electronic character, switching between half-metallic and metallic states depending on pressure. This comparison underscores Mn_3Ru 's stability as a metallic conductor and Cr_3Ru 's versatility for pressure-controlled spin-dependent transport, making the latter particularly promising for functional applications such as spintronics.

In summary, the comparison of Mn_3Ru and Cr_3Ru across the A15, D0c, and tP16 phases under pressure highlights distinct electronic and magnetic behaviors shaped by crystal structure and compression. Mn_3Ru generally exhibits robust metallic conduction, with half-metallicity appearing only in the A15 phase at ambient conditions and gradually collapsing under pressure as band broadening reduces spin polarization. In contrast, Cr_3Ru shows more tunable properties: metallic in A15 and D0c phases but switching between half-metallic and metallic states in the tP16 phase depending on pressure, reflecting the delicate balance between exchange interactions and electron delocalization. The D0c phase for both alloys is consistently metallic, while the tP16 phase demonstrates the strongest pressure-driven transitions, especially for Cr_3Ru . Overall, Mn_3Ru offers stability and reliable metallic conductivity, making it suitable for high-temperature structural applications, whereas Cr_3Ru provides pressure-controlled spin-dependent transport, which could be exploited in functional devices such as spintronics or adaptive conductors. This comparative analysis underscores how phase selection and pressure conditions critically determine the electronic and magnetic performance of these alloys.

5.3.3 Hybridization and bonding characteristics

Mn_3Ru and Cr_3Ru alloys across the A15, D0c, and tP16 phases under zero and varying pressures. In the A15 phase, the density of states (DOS) at the Fermi level is relatively low at zero pressure but increases under compression, reflecting enhanced metallicity. In the D0c phase, Mn_3Ru ,

Cu_3Ru , and Zn_3Ru alloys show lower DOS at E_F , while in the tP16 phase, Cr_3Ru , Mn_3Ru , and Zn_3Ru also exhibit reduced DOS at E_F . This reduction is linked to strong hybridization between Mn/Cr d-orbitals and Ru d-orbitals, which separates bonding from antibonding states and lowers the available states at E_F . The correlation between low DOS at E_F and lower heats of formation (e.g., Mn_3Ru in A15: -0.64 eV/atom; D0c: -1.61 eV/atom; tP16: -1.61 eV/atom at zero pressure) confirms greater thermodynamic stability. Thus, alloys with reduced $N(E_F)$ are more stable, as fewer electronic states at the Fermi level minimize instability from electron–electron interactions.

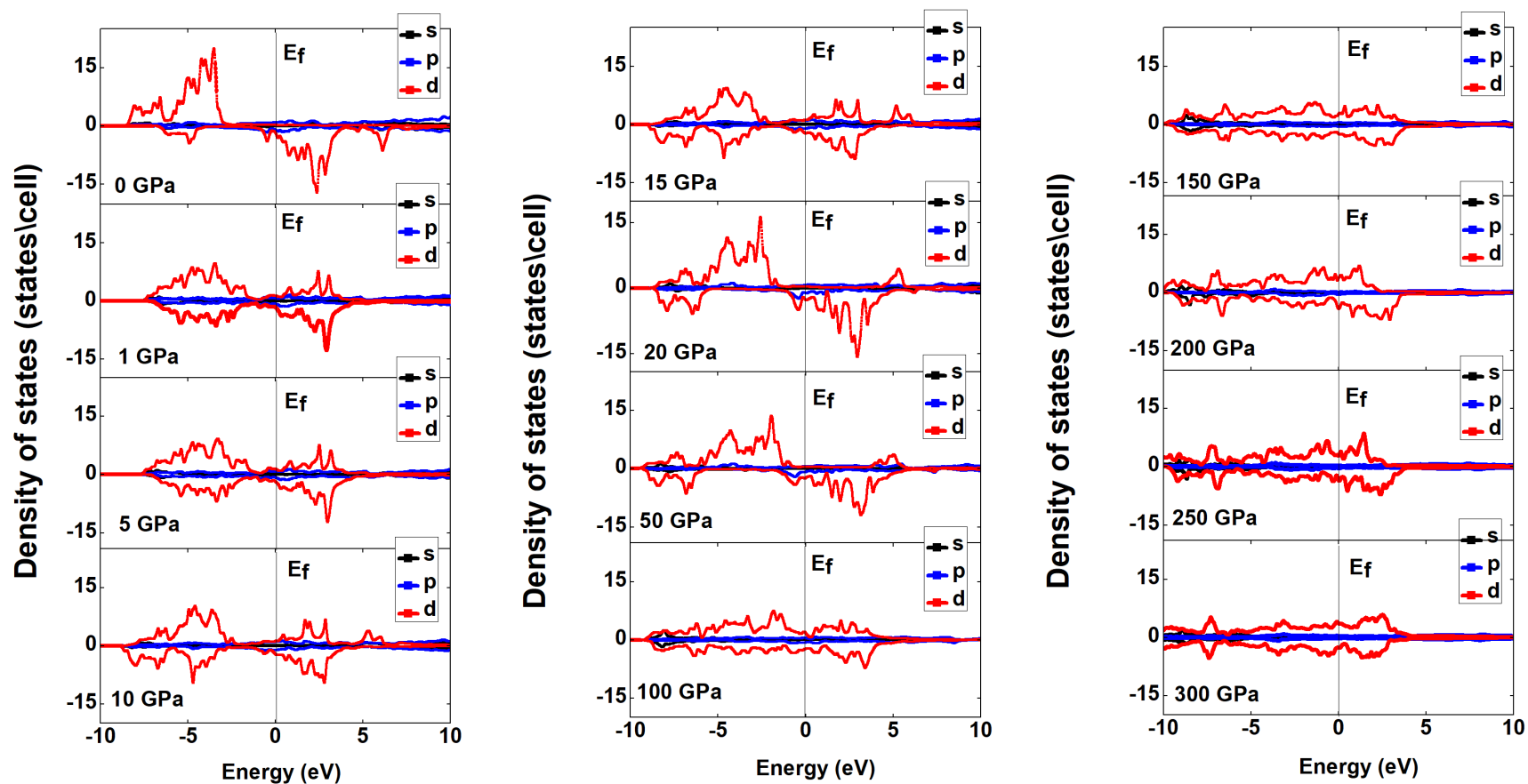


Figure 5.6: Projected spin polarized density of states for A15 Mn_3Ru structures under 0-300 GPa. The Fermi level at 0 eV is represented by a vertical dashed line.

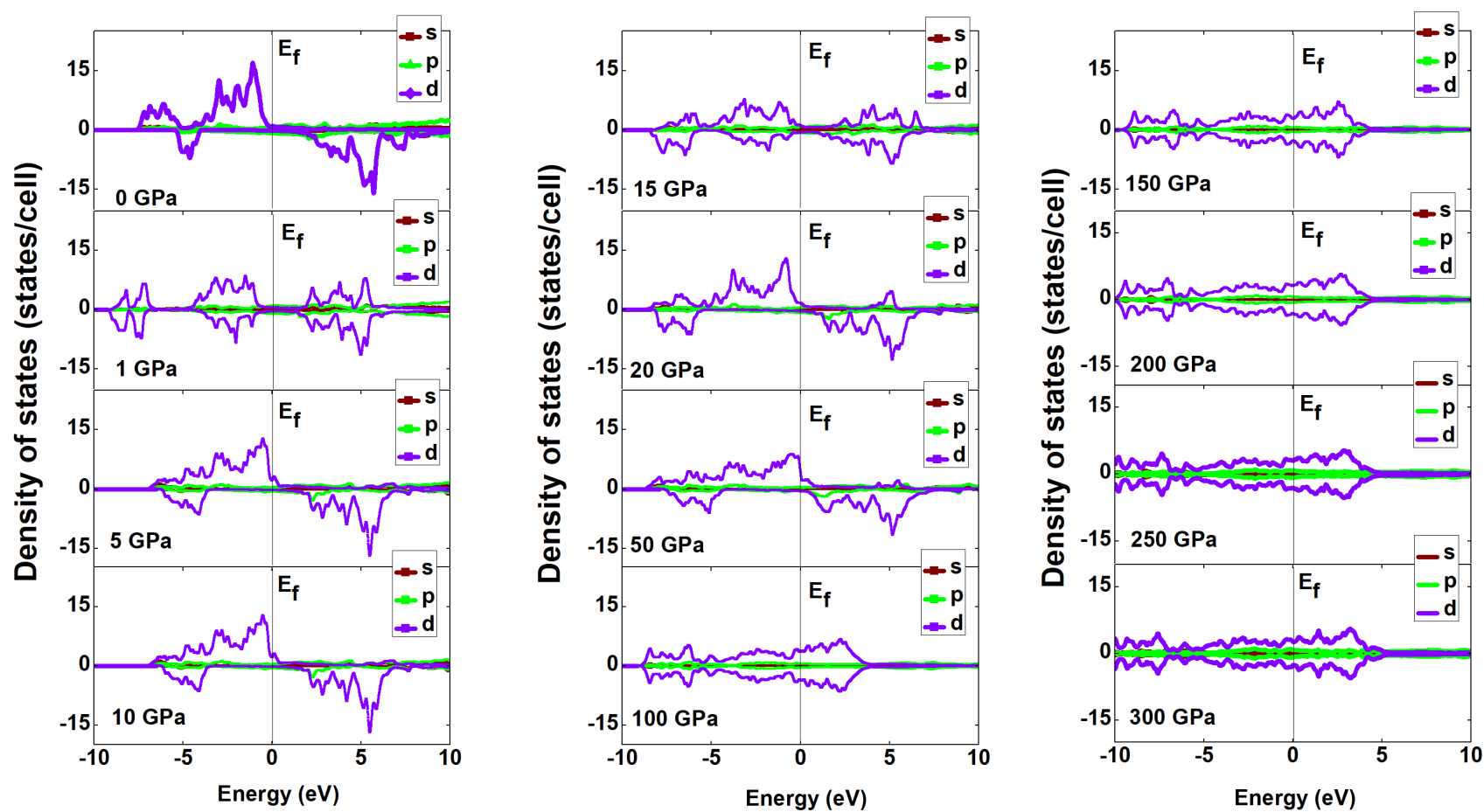


Figure 7.5: Projected spin polarized density of states for A15 Cr₃Ru structures under 0-300 GPa. The Fermi level at 0 eV is represented by a vertical dashed.

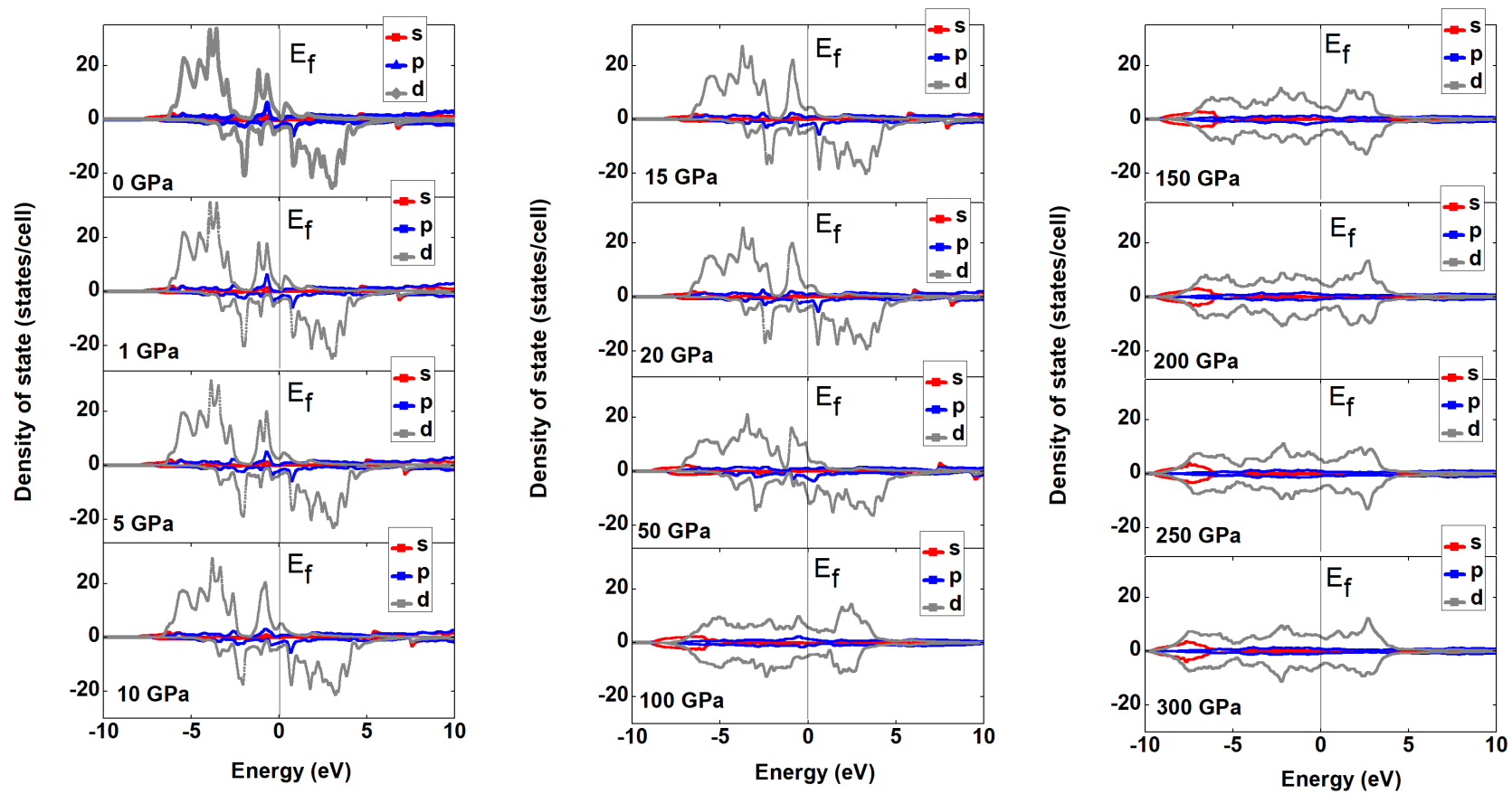


Figure 5.8: Projected spin polarized density of states for D0c Mn_3Ru structures. The Fermi level at 0 eV is represented by a vertical dashed line.

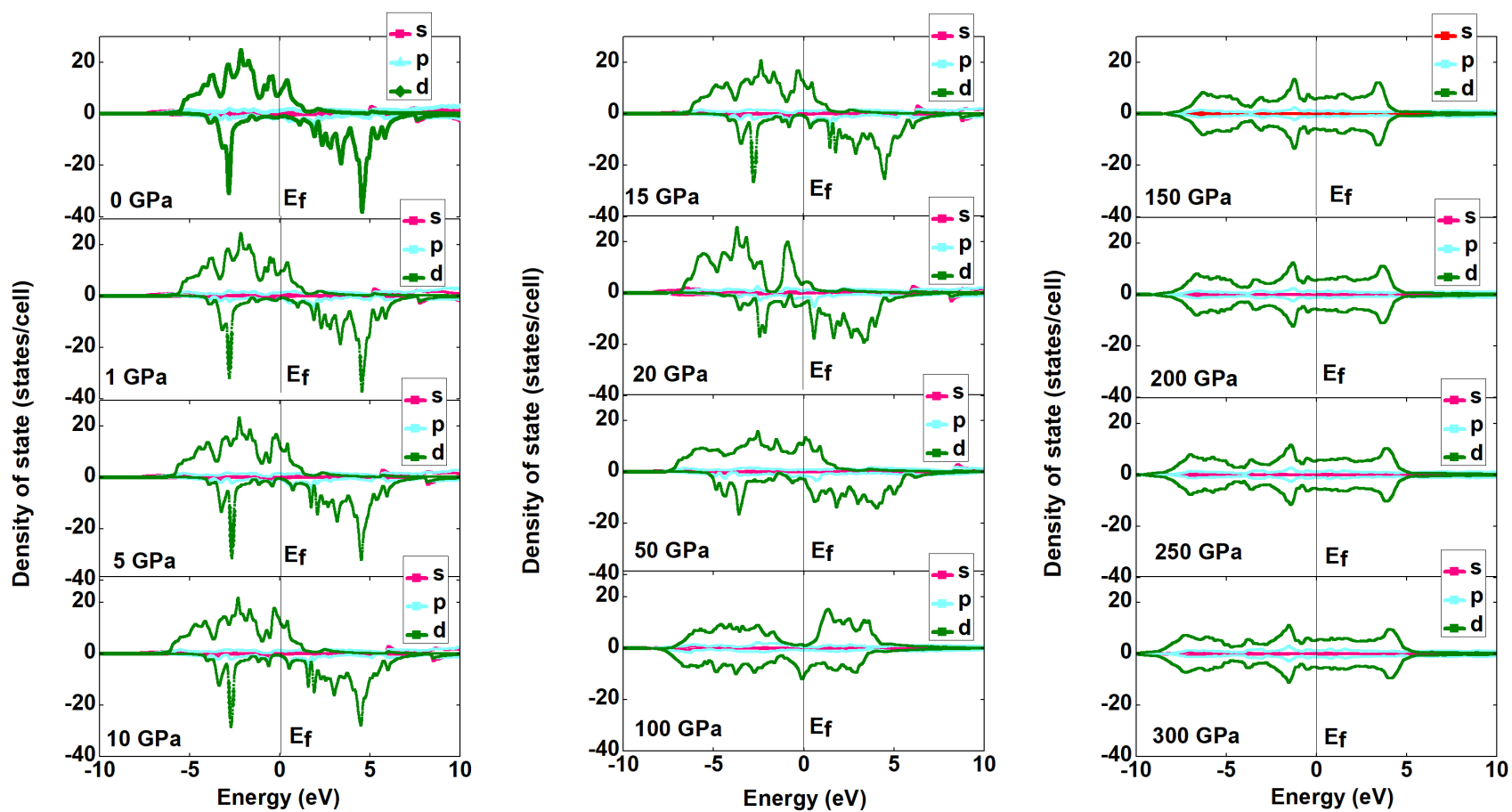


Figure 5.9: Projected spin polarized density of states for D0c Cr_3Ru structures. The Fermi level at 0 eV is represented by a vertical dashed line.

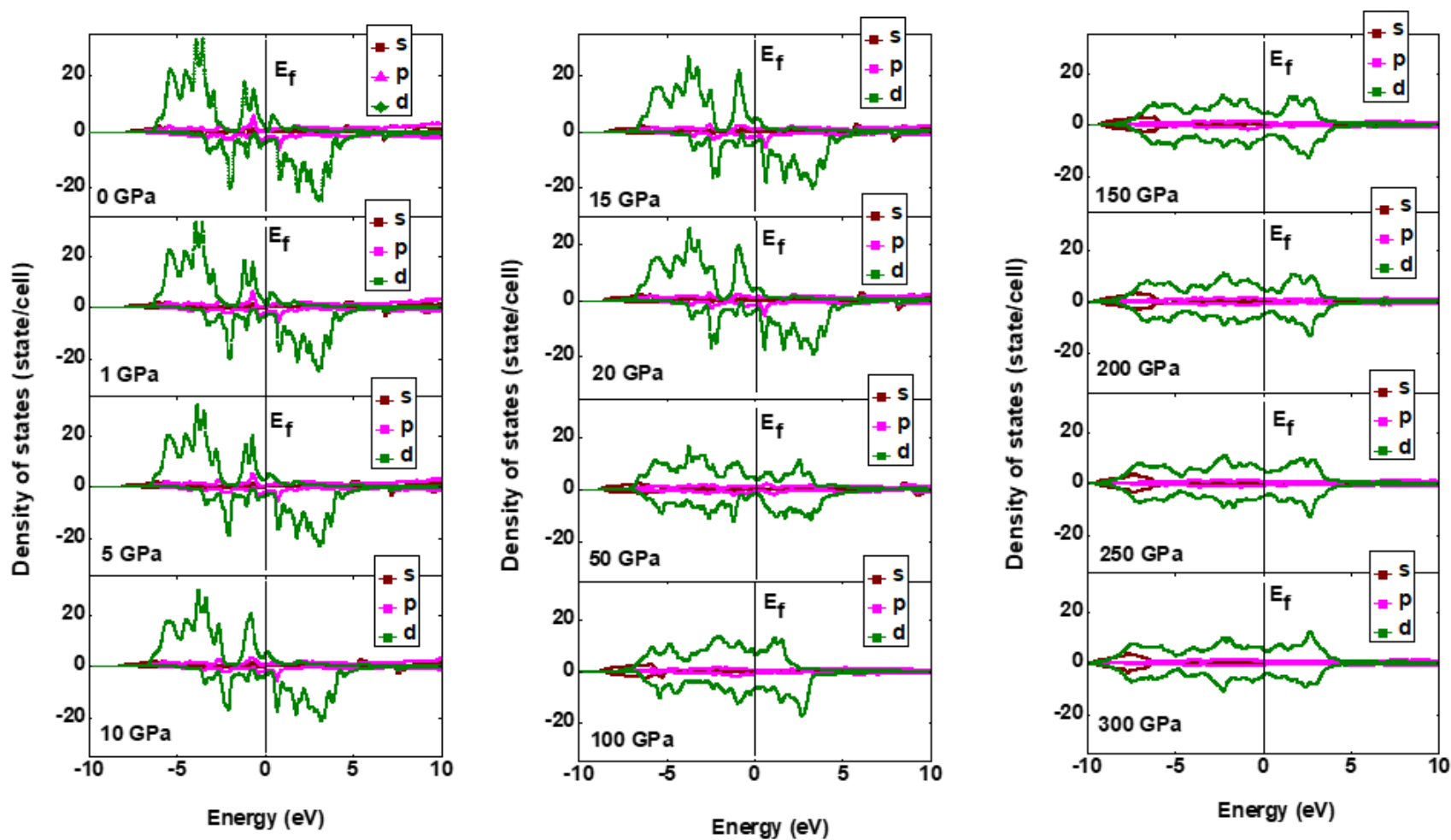


Figure 5.10: Projected spin polarized density of states for tP16 Mn_3Ru structures under pressure (0-300 GPa). The Fermi level at 0 eV is represented by a vertical dashed line.

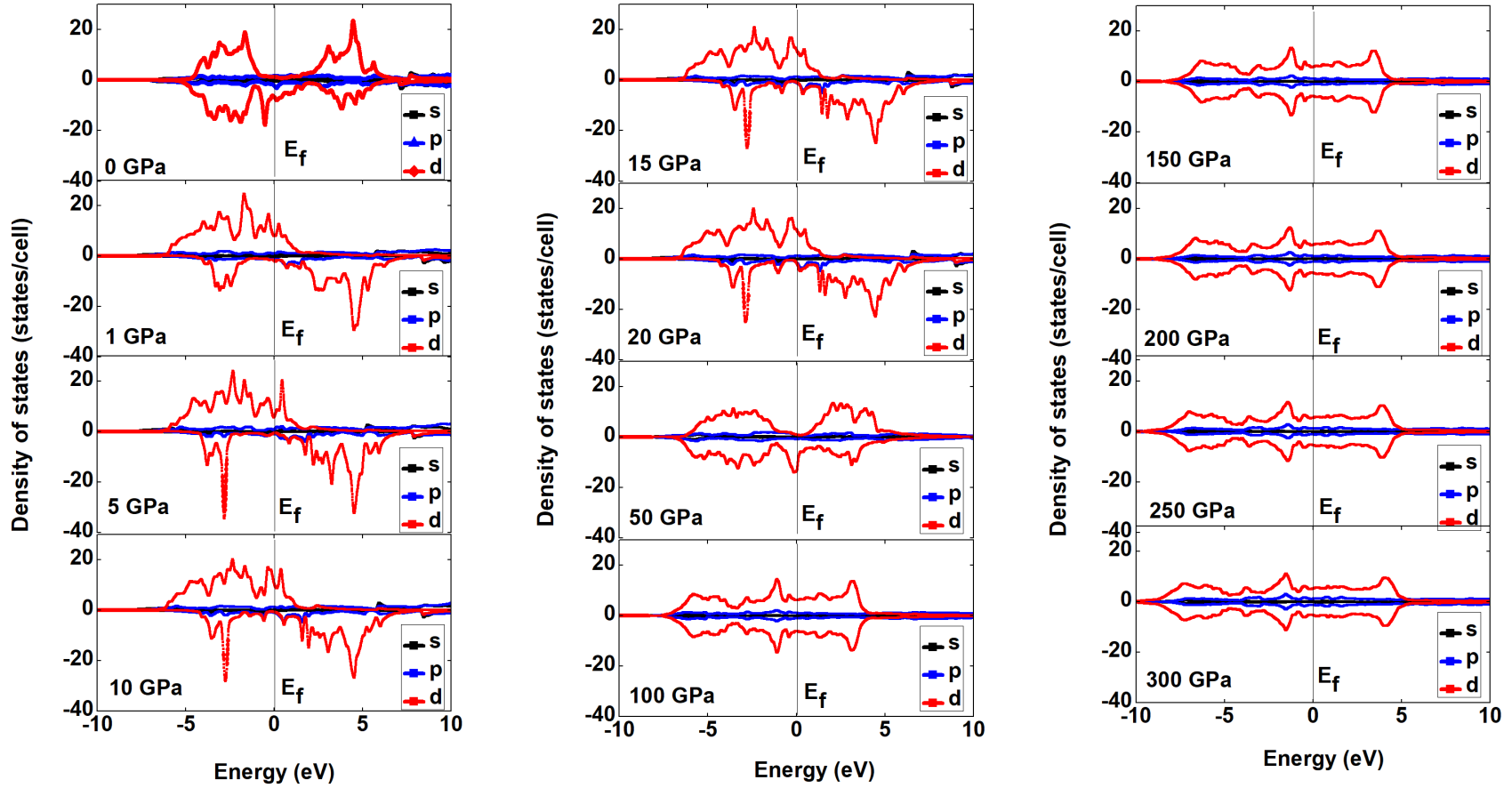


Figure 5.11: Projected spin polarized density of states for tP16 Cr_3Ru structures under pressure (0-300 GPa). The Fermi level at 0 eV is represented by a vertical dashed line.

5.4 Mechanical properties

For D0c and tP16 tetragonal and A15 cubic crystals subjected to pressure, the conditions for mechanical stability [350] are established as similar to those described in chapter 4. The elastic constants (C_{ij}) calculated for the A15, D0c, and tP16 phases of Mn_3Ru and Cr_3Ru alloys under fixed and varying pressure conditions are summarized in Tables 5.6–5.11. For Mn_3Ru in A15 phase at 0 GPa, C_{11} , C_{12} , and C_{44} are 145 GPa, 48 GPa, and -4 GPa, respectively. This compound is mechanically unstable due to negative value of C_{44} , as the lattice cannot resist shear deformation. This instability arises from insufficient restoring forces, allowing shear distortions to occur spontaneously. Between 1 GPa and 50 GPa, the structure remains mechanically unstable due to negative values of C_{12} and C_{44} . However, at higher pressures (100–300 GPa), all elastic constants become positive, fulfilling the mechanical stability criteria outlined in Chapter 4 (Equation 4.5). Thus, Mn_3Ru transitions from mechanically unstable at low pressures to mechanically stable at high pressures.

For Cr_3Ru in the A15 phase at 0 GPa, the elastic constants C_{11} , C_{12} , and C_{44} are 336 GPa, 245 GPa, and 4 GPa, respectively. All values are positive and satisfy the Born mechanical stability criteria (Equation 4.5) for cubic systems, indicating that the structure is mechanically stable at ambient pressure. However, between 1 GPa and 50 GPa, the structure becomes mechanically unstable due to negative values of C_{12} and C_{44} , which reflect the lattice's inability to resist shear and certain strain modes. At higher pressures (100–300 GPa), all elastic constants return to positive values, fulfilling the mechanical stability criteria and restoring structural stability.

For Mn_3Ru in the D0c phase at 0 GPa, the elastic constants C_{11} , C_{12} , C_{44} , C_{66} , and C_{33} are 175 GPa, 17 GPa, 78 GPa, 27 GPa, and 130 GPa, respectively. These values satisfy the Born stability criteria, confirming that the structure is mechanically stable at ambient pressure. The alloy remains stable under moderate pressures (1–20 GPa) and again at very high pressures (150–300 GPa). However, in the intermediate pressure range of 50–100 GPa, several elastic constants become negative, indicating mechanical instability as outlined in Chapter 4 (Equation 4.6). This instability arises because negative elastic constants reflect the lattice's inability to resist shear or certain strain modes, meaning the restoring forces against deformation are insufficient. At higher pressures, compression strengthens interatomic bonding and orbital overlap, restoring positive elastic constants and stabilizing the lattice.

Table 5.7: The calculated elastic constants for A15 Mn₃Ru. All the elastic constants are in GPa under zero and varying pressure conditions.

Mn ₃ Ru Pressure	C ₁₁	C ₁₂	C ₄₄
0	145	48	-4
1	5	-245	-29
5	93	-492	19
10	177	-63	-236
15	280	121	-570
20	184	-3.9	-621
50	261	49	-706
100	1241	1146	48
150	1231	432	76
200	1494	550	72
250	1946	833	96
300	2297	1012	85

Table 5.8: The calculated elastic constants for A15 Cr₃Ru. All the elastic constants are in GPa under zero and varying pressure conditions.

Cr ₃ Ru pressure	C ₁₁	C ₁₂	C ₄₄
0	336	245	4
1	148	51	-7
5	108	36	-11
10	143	50	-7
15	177	61	-7
20	-47	283	-14
50	400	150	-287
100	1018	479	116
150	1285	621	114
200	1527	738	152
250	1732	878	134
300	1933	1000	117

Thus, Mn₃Ru in the D0c phase is mechanically stable at zero, low, and very high pressures, but undergoes instability in the intermediate pressure range due to weakened resistance to shear deformation. For Cr₃Ru in the D0c phase at 0 GPa, the elastic constants C₁₁, C₁₂, C₄₄, C₆₆, and C₃₃ are 78 GPa, -36 GPa, 55 GPa, 0.8 GPa, and 55 GPa, respectively. The negative value of C₁₂ indicates mechanical instability, as the lattice cannot adequately resist strain along certain directions. This instability arises because the restoring forces against deformation are insufficient, allowing distortions to occur spontaneously.

Table 5.9: The calculated elastic constants for D0c Mn₃Ru. All the elastic constants are in GPa under zero and varying pressure.

Mn ₃ Ru	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆
0	175	17	77	130	78	27
1	194	29	86	139	81	27
5	203	26	99	150	90	24
10	251	44	131	182	102	23
15	270	69	155	155	99	11
20	273	55	143	160	108	14
50	276	23	240	107	128	-46
100	2148	1600	1640	1295	293	-255
150	2403	1526	1556	918	408	108
200	1486	410	786	1239	496	723
250	1748	461	951	1510	596	217
300	2103	657	1182	1733	672	257

Table 5.10: The calculated elastic constants for D0c Cr₃Ru. All the elastic constants are in GPa under zero and varying pressure conditions.

Cr ₃ Ru	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆
0	78	-36	16	55	55	0.8
1	116	-6	42	61	56	-8
5	199	51	94	131	74	32
10	235	68	126	146	84	31
15	221	28	86	231	95	27
20	275	71	147	219	109	45
50	428	80	193	361	176	57
100	535	371	366	694	196	232
150	1196	494	747	974	353	85
200	1387	620	884	1085	427	85
250	1542	771	1036	1271	406	127
300	1731	877	1197	1304	481	108

However, under applied pressures between 5 GPa and 300 GPa, all elastic constants become positive, satisfying the Born mechanical stability criteria (Equation 4.5) for tetragonal systems and confirming mechanical stability. Interestingly, at 1 GPa the structure remains unstable, reflecting a transitional regime where pressure is not yet sufficient to suppress shear instabilities. For Mn₃Ru in the tP16 phase at 0 GPa, the elastic constants C₁₁, C₁₂, C₄₄, C₆₆, and C₃₃ are 191 GPa, 29 GPa, 78 GPa, 25 GPa, and 131 GPa, respectively. These values satisfy the Born stability criteria, confirming mechanical stability at ambient pressure.

Table 5.11: The calculated elastic constants for tP16 Mn₃Ru. All the elastic constants are in GPa under zero and varying pressure conditions. All the elastic constants are in GPa.

Mn ₃ Ru	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆
0	191	29	84	131	78	25
1	196	32	89	139	83	26
5	234	58	117	146	92	25
10	267	67	149	160	103	22
15	266	64	157	131	106	11
20	285	67	166	175	113	11
50	309	-0.72	154	181	164	10
100	-3213	-3789	-3066	-3554	305	-194
150	1216	325	595	978	408	110
200	1498	402	778	1440	502	-20
250	2290	1025	1397	1087	587	-9
300	2100	641	1204	3081	677	221

Table 5.12: The calculated elastic constants for tP16 Cr₃Ru under zero and varying pressure conditions. All the elastic constants are in GPa.

Cr ₃ Ru	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆
0	52	36	53	5	-4	16
1	75	36	123	116	90	68
5	223	91	23	131	50	29
10	196	33	80	127	72	37
15	249	57	109	200	97	42
20	268	65	125	215	101	41
50	94	261	146	25	157	186
100	953	377	587	751	282	69
150	1171	471	742	988	327	44
200	1365	639	883	1081	402	102
250	1606	699	1049	1270	445	96
300	1804	799	1204	1381	509	172

The alloy remains stable under moderate pressures (1–20 GPa) and again at very high pressures (150 and 300 GPa). However, in the intermediate pressure ranges of 50, 100, and 200–250 GPa, several elastic constants become negative, indicating mechanical instability as outlined in Chapter 4 (Equation 4.6). This instability occurs because negative elastic constants signify the lattice's inability to resist shear or certain strain modes, meaning the restoring forces against deformation are insufficient. At higher pressures, compression enhances interatomic bonding and orbital overlap, restoring positive elastic constants and stabilizing the lattice. Thus, Mn₃Ru in the tP16 phase is mechanically stable at zero, low, and very high pressures, but undergoes instability in the intermediate pressure range due to weakened shear resistance.

For Cr_3Ru in the tP16 phase at 0 GPa, the elastic constants C_{11} , C_{12} , C_{44} , C_{66} , and C_{33} are 52 GPa, -36 GPa, -4 GPa, 16 GPa, and 5 GPa, respectively. The negative value of C_{44} indicates mechanical instability, as the lattice cannot adequately resist strain along certain directions. This instability arises because the restoring forces against deformation are insufficient, allowing distortions to occur spontaneously. However, under all applied pressures elastic constants become positive, satisfying the Born mechanical stability criteria (Equation 4.5) for tetragonal systems and confirming mechanical stability. Interestingly, at 1 GPa the structure remains unstable, reflecting a transitional regime where pressure is not yet sufficient to suppress shear instabilities.

Across the A15, D0c, and tP16 phases (Figure 5.10), Mn_3Ru and Cr_3Ru alloys display distinct pressure-dependent mechanical stability. For Mn_3Ru , the A15 phase is unstable at ambient and low pressures due to negative shear constants but becomes stable at high pressures (100–300 GPa) as compression strengthens bonding. In the D0c and tP16 phases, Mn_3Ru is stable at zero and low pressures, loses stability in intermediate ranges where negative elastic constants emerge, and regains stability under extreme compression, reflecting a non-monotonic response to pressure. In contrast, Cr_3Ru shows instability in the A15 phase at 0 GPa and at 1 GPa due to negative C_{12} but stabilizes consistently from 5–300 GPa as pressure enhances orbital overlap and lattice stiffness. For Cr_3Ru in D0c and tP16 phases, instability dominates at low pressures, while stability is restored at higher pressures.

Overall, Mn_3Ru exhibits alternating stable and unstable regimes depending on pressure, whereas Cr_3Ru tends to stabilize more reliably under compression. This highlights the critical role of pressure in tuning interatomic bonding and shear resistance, directly governing the mechanical resilience of these alloys.

5.4.1 Bulk, Shear and Young's moduli

The bulk modulus, shear modulus, and Young's modulus are fundamental indicators of a material's elastic behavior, each describing its response to different types of deformation under applied forces. Understanding these moduli is essential not only for selecting suitable materials in engineering applications but also for designing structures capable of withstanding real-world mechanical stresses.

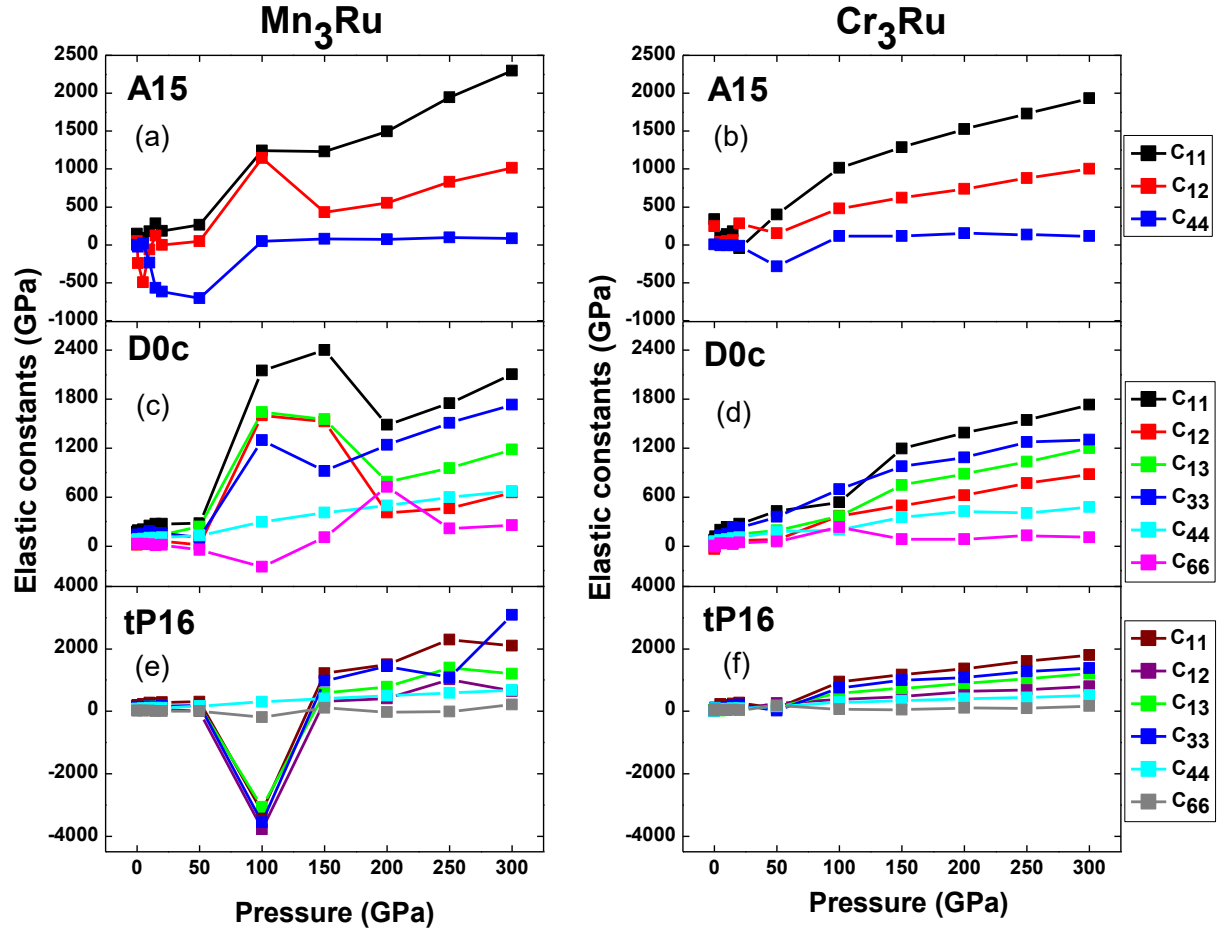


Figure 5.12: Pressure dependences of the elastic constants for A15, D0c and tP16 X_3Ru ($X= Mn$ and Cr) structures.

In this section, the results for the bulk, shear, and Young's moduli of Mn_3Ru and Cr_3Ru alloys in the A15, D0c, and tP16 crystallographic phases under varying pressures are discussed.

5.4.1.1 Bulk modulus

The bulk modulus describes a material's resistance to uniform compression, indicating its ability to withstand changes in volume under applied pressure. For the cubic A15 phase and the tetragonal D0c and tP16 phases, the definitions of the bulk modulus are provided in Chapter 4. In Table 5.11-5.16, we present the calculated bulk (B) modulus, shear (G) modulus, and Young's modulus, the bulk to shear modulus ratio, Poisson's ratio, Cauchy pressure ($C_{12}-C_{44}$), melting temperature and elastic anisotropy for the A15, D0c and Mn_3Ru and Cr_3Ru alloys under zero and varying pressure conditions. In the A15 phase, Mn_3Ru and Cr_3Ru exhibit different bulk modulus behaviors under pressure. For A15 Mn_3Ru , the bulk modulus at zero pressure is 80 GPa, reflecting moderate resistance to compression. With increasing pressure,

the modulus generally rises at 15 GPa, 50 GPa, and in the range of 100–300 GPa, reaching its maximum at 300 GPa. However, at 10 GPa and 20 GPa, the modulus decreases, indicating a temporary softening of the lattice due to weakened restoring forces. This non-monotonic trend highlights how pressure modifies interatomic bonding: intermediate pressures reduce stability, while higher compression enhances orbital overlap and restores stiffness (as shown in Figure 5.11). In contrast, Cr₃Ru in the A15 phase has a bulk modulus of 275 GPa at zero pressure, showing a stiff and incompressible lattice at ambient conditions. Under low pressures (1–20 GPa), the modulus decreases, reflecting lattice softening, but at higher pressures (100–300 GPa) it increases steadily, reaching its maximum at 300 GPa. This continuous strengthening arises from enhanced Cr–Ru orbital overlap and bonding under compression. Thus, Mn₃Ru demonstrates a pressure-dependent softening effect before stabilizing at high pressures, whereas Cr₃Ru shows a smoother stiffening response, evolving from a softened state at low pressures to maximum incompressibility under extreme compression.

In the D0c phase, Mn₃Ru and Cr₃Ru exhibit different compressibility behaviors under pressure. For Mn₃Ru, the bulk modulus at zero pressure is 91 GPa, indicating moderate resistance to uniform compression. With increasing pressure, the modulus rises and reaches its maximum value at 150 GPa, reflecting the strengthening of interatomic bonding as atoms are forced closer together, which enhances orbital overlap and increases the lattice's resistance to volume change.

Table 5.13: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Voigt, Reuss and Hill approximations, Poisson ratio, for A15 Mn₃Ru. All the elastic moduli are in GPa, The melting temperature (K) and universal elastic anisotropy under zero and varying pressure conditions.

Mn ₃ Ru	B _H	G _H	E _H	B _H /G _H	ν	T _m (K)	A ^U
0	80	5	14	16.0	0.48	1410	-17.14
1	-162	12	-35	-3.8	0.46	583	-8.89
5	-297	79	261	-3.8	0.65	1103	15.33
10	17	584	143	0.03	-0.89	1599	-6.37
15	174	-29	-93	-6.0	0.59	2208	-12.15
20	59	-16	-51	-3.7	0.64	1640	-11.51
50	120	-19	-62	-6.3	0.59	2096	-11.57
100	1178	48	142	25	0.48	7887	-1.00
150	698	159	444	4.4	0.39	7828	3.12
200	865	171	480	5.01	0.41	9383	4.64
250	1204	211	599	5.71	0.42	12054	4.80
300	1441	219	625	6.58	0.43	14128	6.85

Table 5.14: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Hill approximation, Poisson ratio, Cauchy pressure (C_{12} - C_{44}), melting temperature (K) and universal elastic anisotropy for A15 Cr₃Ru. The under zero and varying pressure conditions.

Cr ₃ Ru	B _H	G _H	E _H	B/G	ν	T _m (K)	A ^U
0	275	14	40	19.64	0.48	2539	11.50
1	83	63	63	4.37	0.50	1428	-10.45
5	60	-8	-25	-51.9	0.56	1191	-8.67
10	51	1	3	85.26	0.49	1398	10.50
15	99	3	9	33	0.49	1599	-12.26
20	173	-49	-161	-3.53	0.66	275	11.62
50	233	390	751	0.60	0.82	2917	-7.68
100	659	164	454	4.02	0.39	6569	-0.11
150	842	178	499	4.73	0.40	8147	0.48
200	1001	225	628	4.45	0.40	9578	0.19
250	1163	218	617	5.33	0.41	10789	1.80
300	1311	212	604	6.18	0.42	11977	2.67

In contrast, D0c Cr₃Ru has a bulk modulus of only 22 GPa at zero pressure, showing that the lattice is relatively soft and easily compressible under ambient conditions. Under compression, however, the bulk modulus increases steadily, reaching its maximum at 300 GPa (as shown in Figure 5.11). This trend highlights how pressure progressively strengthens Cr–Ru bonding, transforming the lattice from weakly incompressible at ambient conditions into a highly robust and stiff structure under extreme compression.

Table 5.15: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Hill approximation and Poisson ratio all the elastic moduli are in GPa. We also calculate the melting temperature (K) and universal elastic anisotropy for D0c Mn₃Ru under zero and varying pressure conditions.

Mn ₃ Ru	B _H	G _H	E _H	B _H /G _H	ν	T _m (K)	A ^U
0	91	50	126	1.8	0.27	1074	0.63
1	104	52	134	2.0	0.28	1145	0.82
5	111	52	136	2.13	0.30	1188	1.50
10	144	57	150	2.53	0.33	1380	3.46
15	158	39	108	4.05	0.39	1397	16.07
20	153	49	133	3.12	0.35	1413	7.51
50	186	-193	-889	-0.21	1.30	1343	-5.12
100	2030	-140	430	-14.5	0.54	8741	-6.71
150	2180	428	1206	5.01	0.41	8940	-3.24
200	907	451	1161	2.01	0.29	6671	-3.80
250	1078	410	1091	2.63	0.33	7863	1.34
300	1330	461	1240	2.9	0.34	9263	1.31

Table 5.16: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Hill approximation and Poisson ratio all the elastic moduli are in GPa. We also calculate the melting temperature (K) and universal elastic anisotropy for D0c Cr₃Ru under zero and varying pressure conditions.

Cr ₃ Ru	B _H	G _H	E _H	B/G	ν	C ₁₂ -C ₄₄	T _m (K)	A ^U
0	22	20	46	1.10	0.14	-91	671	41.34
1	50	162	233	0.31	-0.28	-62	794	-4.39
5	112	49	129	2.23	0.31	-23	1148	1.40
10	139	48	129	2.90	0.34	-16	1278	2.99
15	118	67	168	1.76	0.26	-67	1364	1.48
20	166	71	186	2.34	0.31	-38	1508	1.45
50	238	118	305	2.02	0.29	-96	2180	1.29
100	438	158	423	2.77	0.34	175	3000	0.76
150	816	210	579	3.89	0.38	141	5403	2.40
200	959	231	642	4.15	0.39	193	6143	2.13
250	1116	249	696	4.48	0.40	365	6887	1.88
300	1253	241	679	5.20	0.41	396	7503	4.35

Thus, D0c Mn₃Ru demonstrates moderate stiffness with peak incompressibility at intermediate pressures, while D0c Cr₃Ru comes from a soft lattice to maximum incompressibility under very high pressures. In the tP16 phase, Mn₃Ru and Cr₃Ru exhibit distinct compressibility behaviors under pressure. For tP16 Mn₃Ru, the bulk modulus at zero pressure is 101 GPa, indicating moderate resistance to uniform compression. With increasing pressure, the modulus generally rises but shows a noticeable decrease at 100 GPa, reflecting a temporary softening of the lattice. Beyond this point, it increases again, reaching its maximum value at 300 GPa (as shown in Figure 5.11). This non-monotonic trend highlights how intermediate pressures weaken restoring forces against volume change, while extreme compression enhances orbital overlap and strengthens bonding, making the lattice highly incompressible. In contrast, Cr₃Ru in the tP16 phase has a bulk modulus of 44 GPa at zero pressure, showing that the lattice is relatively soft and easily compressible under ambient conditions. Under compression, however, the modulus rises steadily without intermediate softening, reaching its maximum at 300 GPa. This behavior reflects a continuous strengthening of Cr–Ru bonding as atoms are forced closer together, progressively increasing resistance to compression. Thus, tP16 Mn₃Ru demonstrates a pressure-dependent softening effect before stabilizing at high pressures, whereas tP16 Cr₃Ru shows a smoother and more consistent stiffening response under compression. Overall, Mn₃Ru exhibits pressure-dependent softening effects in intermediate ranges before stabilizing at high compression, whereas Cr₃Ru shows a more consistent and gradual stiffening trend, evolving from relatively soft at ambient conditions to highly incompressible under extreme pressure.

5.4.1.2 Shear modulus

In the A15 phase of Mn_3Ru , the shear modulus at zero pressure is 5 GPa, indicating very low resistance to shear deformation. Under compression, the modulus generally increases, except in the range of 15–50 GPa where a reduction occurs. The maximum shear modulus is observed at 10 GPa, reflecting a temporary strengthening of the lattice against shear forces. This non-monotonic behavior arises because pressure modifies interatomic bonding: at low pressures, enhanced orbital overlap between Mn and Ru atoms momentarily increases shear resistance, while at intermediate pressures weakened restoring forces reduce stiffness. At higher pressures, bonding interactions strengthen again, leading to an overall increase in shear modulus (as shown in Figure 5.11). In contrast, Cr_3Ru in the A15 phase has a shear modulus of 14 GPa at zero pressure, showing relatively low resistance to shear deformation compared to its bulk modulus. Under compression, the shear modulus generally increases, except at 5 GPa and 20 GPa where reductions occur, indicating temporary lattice softening. The maximum shear modulus is obtained at 50 GPa, reflecting peak resistance to shear forces. Physically, this trend highlights how pressure alters Cr–Ru bonding: at low pressures, weakened restoring forces reduce stiffness, while at moderate pressures enhanced orbital overlap strengthens bonding interactions, producing maximum shear resistance. Overall, Mn_3Ru exhibits a highly sensitive, non-monotonic shear response under pressure, whereas Cr_3Ru shows a more stable stiffening trend with localized instabilities, both reflecting the complex interplay between bonding and lattice stability in the A15 phase.

In the D0c phase of Mn_3Ru , the shear modulus at zero pressure is 50 GPa, indicating relatively weak resistance to shear deformation. With compression, the modulus generally increases, though a reduction occurs between 15–100 GPa, suggesting temporary lattice softening. The maximum shear modulus is reached at 300 GPa, reflecting the strongest resistance to shear forces. This non-monotonic behavior arises because pressure modifies interatomic bonding: at intermediate pressures, weakened restoring forces reduce shear stiffness, while at higher compression enhanced orbital overlap between Mn and Ru atoms strengthens bonding interactions, leading to maximum shear resistance. In contrast, Cr_3Ru in the D0c phase begins with a shear modulus of 20 GPa at zero pressure, also indicating weak shear resistance relative to its bulk modulus. Under compression, however, the modulus rises steadily without intermediate softening, reaching its maximum at 249 GPa. This continuous increase reflects the progressive strengthening of Cr–Ru bonding as atoms are forced closer together, enhancing

orbital overlap and making the lattice increasingly resistant to shear deformation. Overall, Mn₃Ru exhibits a non-monotonic shear response with instability at moderate pressures before stiffening at extreme compression, whereas Cr₃Ru shows a general increase in monotonic stiffening trend, both highlighting the distinct pressure-dependent bonding characteristics of these alloys in the D0c phase. In the tP16 phase of Mn₃Ru, the shear modulus at zero pressure is 50 GPa, indicating relatively weak resistance to shear deformation. With compression, the modulus generally increases from 50–300 GPa, though a reduction occurs in the low-pressure range of 1–20 GPa. The maximum shear modulus is reached at 100 GPa, reflecting the strongest resistance to shear forces. This non-monotonic behavior arises because pressure modifies interatomic bonding: at low pressures, weakened restoring forces reduce shear stiffness, while at higher compression enhanced orbital overlap between Mn and Ru atoms strengthens bonding interactions, leading to maximum shear resistance. In contrast, Cr₃Ru in the tP16 phase begins with a negative shear modulus of –7 GPa at zero pressure, indicating mechanical instability and a tendency toward shear deformation.

Table 5.17: The calculated bulk modulus (B), shear modulus (G), Young modulus (E) in Voigt, Reuss and Hill approximations, Poisson ratio for tP16 X₃Ru (X = Cr and Mn). All the elastic moduli are in GPa, The melting temperature (K) and universal elastic anisotropy.

Mn ₃ Ru	B _H	G _H	E _H	B/G	ν	T _m (K)	A ^U
0	101	50	128	2.02	0.29	1124	1.79
1	16	52	133	2.04	0.29	1151	1.81
5	132	51	137	2.57	0.33	1275	2.88
10	157	48	130	3.28	0.36	1395	7.16
15	163	-24	-74	-6.94	0.58	1349	-7.85
20	171	44	142	3.89	0.38	1472	14.45
50	156	61	163	2.56	0.33	1553	17.97
100	-3305	1600	5724	-2.07	0.79	15324	-4.87
150	716	271	723	2.64	0.33	5469	1.75
200	921	119	341	7.73	0.44	7008	-13.46
250	2267	160	468	14.2	0.47	8855	-53.62
300	1422	537	1432	2.65	0.33	11276	1.34
Cr ₃ Ru	B _H	G _H	E _H	B/G	ν	T _m (K)	A ^U
0	44	-7	-20	-6.9	0.58	518	-4.77
1	104	68	168	1.53	0.23	753	-2.48
5	89	52	129	1.72	0.26	1220	0.86
10	10	53	135	1.90	0.28	1133	-0.44
15	139	70	180	1.99	0.28	1401	0.51
20	154	72	186	2.14	0.30	1481	1.00
50	168	-87	-317	-1.93	0.82	674	-6.75
100	640	167	461	3.83	0.38	4340	2.52
150	803	177	494	4.54	0.40	5349	4.47
200	958	230	639	4.17	0.39	6071	2.43
250	1119	250	697	4.17	0.40	7077	3.16
300	1267	289	805	4.38	0.39	7838	3.11

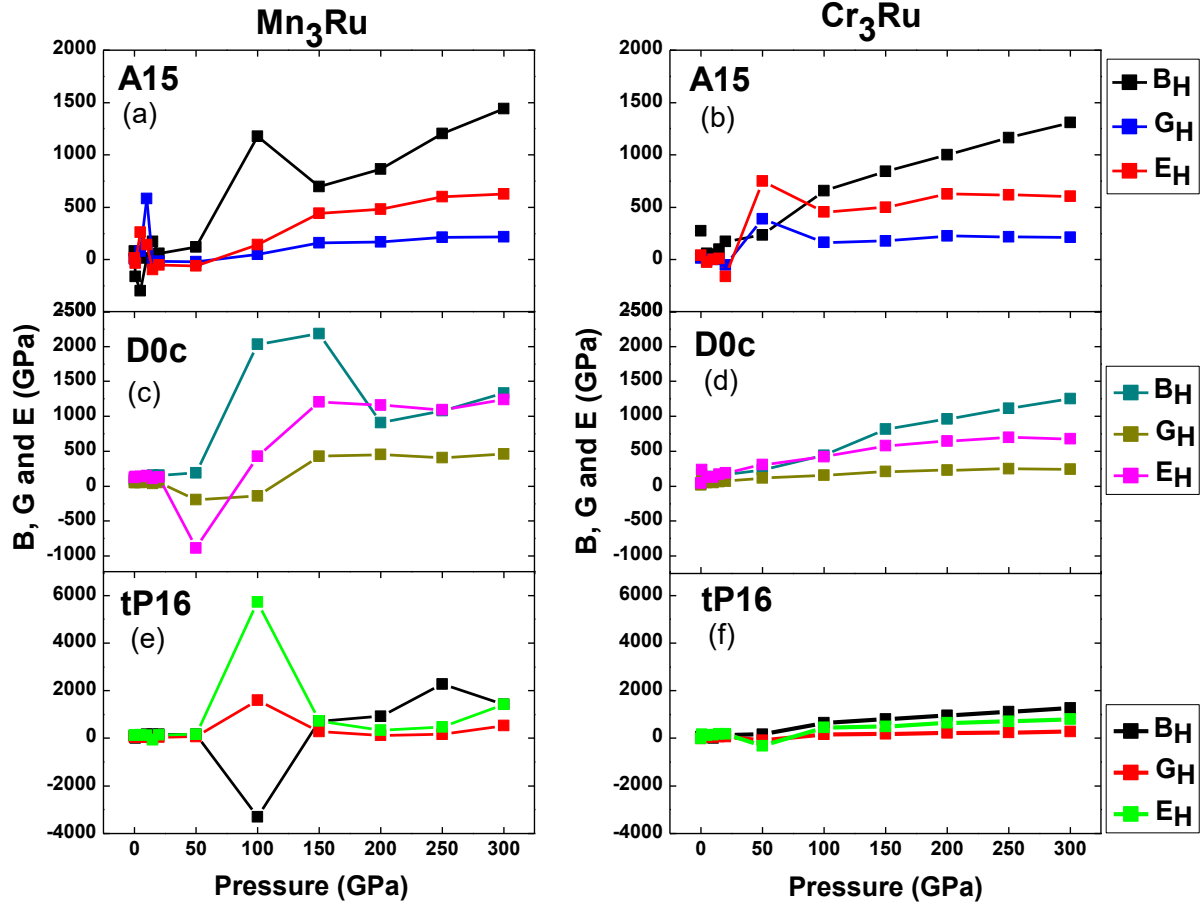


Figure 5.13: Dependences of elastic moduli on the pressures for A15, D0c and tP15 $X_3\text{Ru}$ ($X = \text{Mn}$ and Cr) structures.

Under compression, the modulus rises into positive values between 1–20 GPa, drops again to more negative values at 50 GPa, and then increases monotonically from 100–300 GPa (as shown in Figure 5.11). This progression reflects the stabilization of the lattice under sufficient compression, where enhanced Cr–Ru orbital overlap strengthens bonding and transforms the structure from unstable at ambient conditions into a mechanically robust phase under extreme pressure. Overall, Mn_3Ru shows a non-monotonic but stabilizing shear response, while Cr_3Ru transitions from instability to robustness, highlighting distinct pressure-dependent bonding characteristics in the tP16 phase.

5.4.1.3 Young's modulus

In the A15 phase of Mn_3Ru , the modulus is 14 GPa at zero pressure, reflecting weak stiffness. Under pressure, it increases irregularly at 5–10 GPa, drops to negative values between 15–50 GPa (indicating instability), and then rises monotonically from 100–300 GPa, reaching its

maximum at 300 GPa. In contrast, Cr₃Ru in the A15 phase begins at 40 GPa and increases across most pressure ranges, except for reductions at 5 GPa and 20 GPa, with peak stiffness achieved at 200 GPa.

In the D0c phase, Mn₃Ru exhibits a higher initial modulus of 126 GPa but shows instability with negative values at 15 GPa and 50 GPa before recovering and reaching its maximum at 300 GPa. D0c Cr₃Ru in the same phase starts at 46 GPa and increases steadily under compression, attaining its maximum at 250 GPa.

In the tP16 phase, Mn₃Ru begins at 128 GPa, with a generally increasing trend except for a drop to negative values at 15 GPa and reaches its maximum at 300 GPa. Cr₃Ru, however, starts with a negative modulus of –20 GPa at zero pressure, indicating mechanical instability, but under compression the modulus becomes positive and increases steadily, reaching its maximum at 300 GPa.

Overall, Mn₃Ru phases display non-monotonic behavior with temporary instabilities at intermediate pressures before stiffening under extreme compression, whereas Cr₃Ru phases show more stable and progressive increases, with the tP16 phase transitioning from instability at ambient conditions to robustness at high pressure (as shown in Figure 5.11).

5.4.2 Ductility

Pressure plays a significant role in influencing ductility, as both bulk and shear moduli are pressure-dependent. In the A15 phase of Mn₃Ru, the ratio is 16 at zero pressure, confirming ductility. Under compression, the ratio decreases across most pressures except at 100 GPa, where it rises sharply to 25, marking the highest ductility. In contrast, Cr₃Ru in the A15 phase begins with a ratio of 19.64, also ductile, but shows irregular behavior under pressure: it increases significantly at 10–15 GPa (peaking at 85.26 at 10 GPa), while at 5 GPa it drops to –51.9, indicating instability. Thus, ductility in Cr₃Ru is enhanced in the 10–20 GPa range, whereas Mn₃Ru shows maximum ductility at 100 GPa. In the D0c phase, Mn₃Ru starts with a ratio of 1.8, just above the ductile threshold, and generally increases under pressure except between 50–100 GPa where it becomes negative, indicating brittleness. The highest ductility is observed at 150 GPa. Cr₃Ru in the same phase begins with a ratio of 1.1, suggesting

brittleness at ambient conditions, but increases steadily under compression (except at 1 GPa), indicating enhanced ductility at higher pressures. In the tP16 phase, Mn₃Ru has an initial ratio of 2.02, confirming ductility, and increases across most pressures except at 15 GPa where it drops negative. The maximum ductility is observed at 200 GPa with a ratio of 14.2. Cr₃Ru, however, begins with a negative ratio of -6.9, indicating instability, but transitions to positive values under compression, except at 50 GPa. This transition suggests a brittle-to-ductile shift under pressure, with maximum ductility achieved at 300 GPa. Overall, Mn₃Ru phases exhibit ductile behavior with non-monotonic variations and enhanced ductility at specific pressures, while Cr₃Ru phases show instability at low pressures but progressively transition to ductile behavior under high compression, highlighting the critical role of pressure in governing the ductile–brittle response of these alloys.

5.4.3 Poisson's ratio

Poisson's ratio (ν) provides insight into a material's ductility, with values greater than 0.3 generally indicating ductile behavior. In the A15 phase of Mn₃Ru, Poisson's ratio is above 0.3 at zero pressure, confirming ductility in agreement with the B/G ratio results. Under compression, ν increases at 5, 15, 20, and 50 GPa (0.65, 0.59, 0.64, and 0.59 respectively), with the highest value observed at 15 GPa, while other pressures yield lower ratios. For Cr₃Ru in the A15 phase, Poisson's ratio is 0.48 at zero pressure, also indicating ductility. Under pressure, ν generally increases across 1–20 GPa and at 50 GPa, with the maximum value at 50 GPa, showing enhanced ductility consistent with the B/G ratio. In the D0c phase, Mn₃Ru exhibits a Poisson's ratio below 0.3 at zero pressure, suggesting brittleness and contradicting the B/G ratio. Under compression, ν increases across most pressures except at 5 GPa, with the highest value at 150 GPa, indicating enhanced ductility at higher compression. Cr₃Ru in the D0c phase also begins with $\nu < 0.3$, confirming brittleness, but under pressure the ratio increases steadily (except at 1 GPa), reaching 0.41 at 300 GPa, consistent with the ductility predicted by B/G. In the tP16 phase, Mn₃Ru starts with $\nu < 0.3$, indicating brittleness, but under compression the ratio increases generally (except at 1 GPa), with the highest value at 100 GPa, showing enhanced ductility in agreement with B/G. Cr₃Ru in the tP16 phase begins with a ductile value of 0.58 at zero pressure. Under compression, ν increases at 50 GPa to 0.82, while other pressures show decreases, with the rise at 50 GPa reflecting enhanced ductility. Overall, Mn₃Ru phases show pressure-dependent transitions from brittle to ductile behavior, with ductility

enhanced at specific pressures, while Cr_3Ru phases generally maintain ductility or change from brittle to ductile under compression, confirming the strong correlation between Poisson's ratio and the B/G criterion.

5.4.4 Elastic anisotropy

Investigating elastic anisotropy in crystalline materials provides essential understanding of their mechanical behavior, particularly in how stress is distributed under different loading conditions. This section examines the effect of pressure on the elastic anisotropy of the A15, D0c, and tP16 phases of Cr_3Ru and Mn_3Ru alloys. Pressure serves as a tuning parameter for elastic anisotropy, influencing whether a crystal becomes more directionally stiff or unstable. As a result, pressure is a critical factor in predicting the mechanical reliability of these alloys and their phases when subjected to extreme environments. The elastic anisotropy equations are described in chapter 4 by Ranganathan et al [322].

Tables 5.11–5.16 present the elastic anisotropy values for the A15, D0c, and tP16 phases of X_3Ru ($\text{X} = \text{Mn}$ and Cr) alloys under pressure. In the A15 phase, Mn_3Ru exhibits an anisotropy value of -17.14 at zero pressure, deviating from 0 and 1 and thus confirming anisotropy. Under compression, the values generally increase, with the highest anisotropy observed at 5 GPa (15.33), indicating pronounced directional dependence of its elastic properties. Cr_3Ru in the same phase begins with an anisotropy value of 11.50 at zero pressure, also anisotropic, and shows an increase only at 20 GPa, where the maximum value is obtained, while other pressures yield a general decrease. In the D0c phase, Mn_3Ru has an initial anisotropy value of 0.63, increasing between 1–20 GPa and again from 250–300 GPa, with the highest value at 10 GPa (16.07). At other pressures, the values decrease, reaching a minimum of -6.71 . Cr_3Ru in the D0c phase starts with a high anisotropy of 41.34 at zero pressure, but generally decreases under compression, reaching a minimum of -4.39 , while the maximum anisotropy is recorded at 44.98. In the tP16 phase, Mn_3Ru begins with an anisotropy value of 1.79, confirming anisotropy, and shows increases between 1–10 GPa and 20–50 GPa, with the highest value at 50 GPa, while other pressures yield decreases, including a minimum of -53.62 at 250 GPa. Cr_3Ru in the tP16 phase starts with -4.77 at zero pressure, also anisotropic, and under compression generally increases, except at 50 GPa (-6.75), with the highest anisotropy observed at 150 GPa (4.47). Overall, both Mn_3Ru and Cr_3Ru alloys exhibit strong

pressure-dependent elastic anisotropy across all phases, with values deviating significantly from isotropy and highlighting the directional sensitivity of their mechanical responses under compression.

5.4.5 Melting point temperature

To further understand the properties of $X_3\text{Ru}$ alloys, we investigated the melting temperatures of Cr_3Ru alloy under varying pressure conditions, motivated by experimental observations documented in references [251,351]. Figure 5.12 shows the variation in melting temperatures of the A15, D0c, and tP16 Cr_3Ru and Mn_3Ru alloys under pressure. This section analyzes the effect of pressure on the melting temperature of the A15, D0c, and tP16 phases of Cr_3Ru and Mn_3Ru alloys. At elevated pressures ranging from 150–300 GPa, the melting temperature of these alloys exhibits a linear increase, reflecting enhanced thermal stability under compression. A similar trend is observed in Mn_3Ru , where the melting temperature rises linearly between 250–300 GPa. Interestingly, the tP16 phase of Mn_3Ru displays anomalous behavior, with the highest melting temperature recorded at 100 GPa, suggesting a pressure-induced stabilization unique to this phase (as shown in Table 5.18). Notably, the D0c Cr_3Ru alloy exhibits a consistent rise in melting temperature across both low and high-pressure regimes, distinguishing it from the A15 and tP16 Cr_3Ru alloy phases (as shown in Table 5.19). Under extreme pressures, atomic bonds strengthen and the crystal lattice becomes more stable, requiring greater thermal energy to melt. The observed linear rise in melting temperature reflects how bonding interactions respond to compression, manifesting as macroscopic thermal robustness in high-pressure conditions. These findings imply that external pressure plays a significant role in modulating the melting temperatures of these alloy systems. This pressure-dependent behavior indicates the potential for optimizing the thermal performance of Cr_3Ru and Mn_3Ru alloys in high-temperature applications. Furthermore, the observed trend is consistent with results from previous studies [352], affirming the influence of pressure on phase stability and melting characteristics in metal alloys. Overall, our results suggest that the manipulation of pressure could be a viable strategy for enhancing the operational capabilities of these materials in advanced technological applications.

Table 5.18: The calculated melting temperature T_m under low- and high-pressure conditions for Mn_3Ru in A15, D0c and tP16 phases.

Mn_3Ru	A15 Phase T_m (K)	D0c phase T_m (K)	tP16 phase T_m (K)
0	1410	1074	1124
1	583	1145	1151
5	1103	1188	1275
10	1599	1380	1395
15	2208	1397	1349
20	1640	1413	1472
50	2096	1343	1553
100	7887	8741	15324
150	7828	8940	5469
200	9383	6671	7008
250	12054	7863	8855
300	14128	9263	11276

Table 5.19: The calculated melting temperature T_m under low- and high-pressure conditions for Mn_3Ru in A15, D0c and tP16 phases.

Cr_3Ru	A15 Phase T_m (K)	D0c phase T_m (K)	tP16 phase T_m (K)
0	2539	671	518
1	1428	794	753
5	1191	1148	1220
10	1398	1278	1133
15	1599	1364	1401
20	275	1508	1481
50	2917	2180	674
100	6569	3000	4340
150	8147	5403	5349
200	9578	6143	6071
250	10789	6887	7077
300	11977	7503	7838

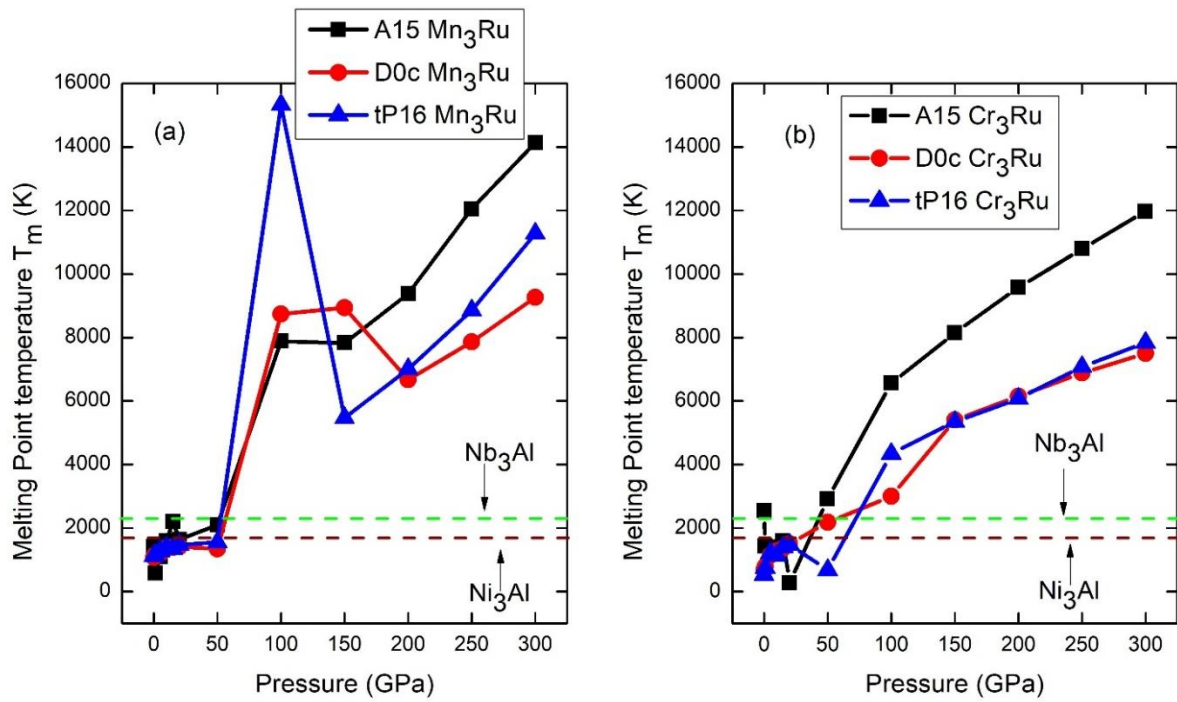


Figure 5.12: The calculated melting temperature T_m under low- and high-pressure conditions for Mn_3Ru and Cr_3Ru in A15, D0c and tP16 phases. The brown dotted line represents Ni_3Al (1691 K) whilst the green dotted line represents Nb_3Al (2333 K).

In summary, the contributions and insights of this study are diverse and impactful. Pressure-induced phase transitions may improve structural stability, thereby enhance ductility and reduce brittleness directly addressing one of the major limitations of Ru-based alloys. Electronic properties are expected to undergo significant changes, as pressure alters orbital overlapping and bonding, which could result in improved conductivity or the emergence of novel magnetic states. The elastic and mechanical response under compression highlights how strengthened interatomic interactions can boost mechanical resistance at elevated temperatures, broadening the applicability of these alloys in extreme environments. Moreover, the magnetic behavior, particularly in Mn_3Ru , can be tuned through pressure, creating opportunities for multifunctional applications that combine mechanical robustness with magnetic performance. Collectively, these aspects provide a pathway to overcome existing challenges while offering new insights into the advancement of Ru-based materials for high-temperature structural and functional applications.

Chapter Six

6.1 Summary and Conclusion

In this thesis, we investigate the structural, electronic and mechanical properties of $X_3\text{Ru}$ alloys ($X=\text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu}$ and Zn) in their A15, D0c and tP16 phases, using the first-principles density functional theory techniques. The limitations of this method have been highlighted in the methodology section. Notably, this is the first comprehensive investigation of these structures, revealing crucial insights into their potential for high- temperature structural applications.

In the A15 $X_3\text{Ru}$ alloys, the calculated heat of formation for Mn_3Ru and Cr_3Ru are negative, indicating thermodynamic stability. Similarly, in the D0c and tP16 phases, the alloys Sc_3Ru , Ti_3Ru , V_3Ru , Mn_3Ru , and Zn_3Ru also exhibit negative heat of formation. These results suggest that these alloys can be synthesized under experimental equilibrium conditions, making them promising candidates for practical applications. In contrast, the remaining systems, which exhibit positive heat of formation, are deemed thermodynamically unstable under equilibrium conditions, although they may be stabilized through non-equilibrium conditions or doping, offering opportunities to develop metastable phases with unique properties.

In the A15 phase, the density of the Mn_3Ru alloy is slightly lower than that of the $\text{L}_{12}\text{-Ni}_3\text{Al}$ alloy which is commonly used in high-temperature structural applications. This trend is also observed in the D0c phase, where Sc_3Ru and Ti_3Ru , have lower densities than $\text{L}_{12}\text{-Ni}_3\text{Al}$. Likewise in the tP16 phase, Sc_3Ru and Ti_3Ru likewise maintain lower densities compared to $\text{L}_{12}\text{-Ni}_3\text{Al}$. These properties position them as promising candidates for high-temperature, lightweight structural applications, such as components in gas turbine engines where minimizing weight while maintaining mechanical strength and thermal resistance is critical. In essence, these alloys offer the potential to improve fuel efficiency, performance, and durability in aerospace and energy systems by serving as next-generation high-temperature structural materials.

In all the $X_3\text{Ru}$ phases, the electronic states are concentrated around the Fermi energy (E_f) level, with no bandgap separating the valence and conduction bands. This characteristic confirms

their metallic nature, enabling a seamless transition of electrons from the valence band to the conduction band, resulting in excellent electrical conductivity. These observations make these alloys suitable for applications where efficient electron transport is critical, such as in electronic devices, conductive coatings, and high-temperature structural components that require both mechanical strength and reliable electrical performance.

Mechanical properties play a crucial role in the design and engineering of high-temperature structural materials. In this study, we analyzed the elastic constants, elastic moduli, bulk-to-shear ratios, Vickers hardness, and melting temperatures of the A15, D0c, and tP16 X_3Ru alloys. Our analysis reveals that in the A15 phase, the Cr_3Ru and Sc_3Ru alloys are mechanically stable. In the D0c phase, most structures are mechanically stable except for the Sc_3Ru , Ti_3Ru , and Cr_3Ru alloys. Similarly, in the tP16 phase, all structures are mechanically stable except for Cr_3Ru and Fe_3Ru alloys, highlighting the varying mechanical stability across different phases of X_3Ru alloys. These findings provide a phase-dependent framework for identifying alloys that exhibit both thermodynamic stability and mechanical strength, thereby guiding experimental synthesis and supporting their application in advanced structural materials.

The bulk-to-shear ratio (B/G) analysis indicates ductile behavior in the A15 phase for Ti_3Ru , Cr_3Ru , Mn_3Ru , and Fe_3Ru . In the D0c and tP16 phases, Sc_3Ru , Mn_3Ru , Fe_3Ru , Co_3Ru , Ni_3Ru , Cu_3Ru , and Zn_3Ru also demonstrate ductility with B/G values exceeding the threshold value of 1.75. The B/G ratios obtained for the A15, D0c, and tP16 phases closely match those of the widely used $L1_2-Ni_3Al$ alloy, indicating that these ductile alloys can endure significant plastic deformation before failure, making them suitable for applications where strength and toughness are required such as gas turbine engines and advanced aerospace systems.

The Vickers hardness analysis shows that in the A15 phase, Fe_3Ru is the hardest alloy, with a hardness index of 3.81 GPa. In the D0c phase, V_3Ru exhibits the highest Vickers hardness at 13.80 GPa, while in the tP16 phase, V_3Ru remains the hardest alloy with a hardness of 8.35 GPa. These high Vickers hardness values indicate their potential for use in applications requiring wear resistance, durability, and mechanical strength under extreme conditions.

Regarding the melting temperatures, In the A15 phase, the calculated melting temperatures (T_m) for Ti_3Ru (6823.51 K), V_3Ru (1983.22 K), Cr_3Ru (2538.76 K), and Co_3Ru (5074.15 K) compare favorably or exceed those of the widely alloys like Ni_3Al (1691 K) [53] and Nb_3Al

(2333 K) [330]. In the D0c phase, the calculated T_m values for Fe_3Ru (1821.44 K), Co_3Ru (1717.64 K), and Ni_3Ru (1756.23 K) meet or surpass these benchmarks. For the tP16 phase, Fe_3Ru (1794.87 K) and Ni_3Ru (1795.19 K) exhibit comparable or higher T_m values than Ni_3Al and Nb_3Al . In addition to the high melting temperatures of these alloys, they also possess a range of other favorable properties including thermodynamic stability, and mechanical stability, positioning them as promising materials for future use in gas turbine engines, aerospace systems, and advanced energy technologies and other high-performance structural applications where heat resistance and mechanical integrity are paramount.

The effect of pressure in this study is examined on selected cases - Cr_3Ru and Mn_3Ru alloys in the A15, D0c, and tP16 phases. The findings demonstrate that pressure significantly influences their thermodynamic, electronic, and mechanical stability. Specifically, Mn_3Ru , which is inherently stable and magnetic under ambient conditions, progressively losing both stability and magnetization under compression, highlighting the limitations of high-pressure synthesis for this alloy. In contrast, Cr_3Ru , unstable at equilibrium, undergoes pressure-induced stabilization in the D0c and tP16 phases, establishing pressure as a critical parameter for enabling equilibrium synthesis of otherwise metastable systems. The observed trends including lattice contraction, increased density, band broadening, and suppression of magnetization provide a coherent framework for understanding how external thermodynamic factors reshape alloy behavior.

Overall, this study addresses the persistent challenges of brittleness and instability in Ru-based alloys by establishing clear design principles for tailoring their structural, electronic, and magnetic properties under extreme conditions. The integration of theoretical modeling with practical synthesis considerations highlights how computational approaches can guide alloy optimization, advance the methodology of computational alloy design and provide a foundation for developing materials capable of withstanding demanding environments.

The novelty of this research lies in identifying Ru-based alloys with remarkable high-temperature durability, mechanical strength, and multifunctional performance, while simultaneously expanding the design space beyond conventional Ni-based systems. These discoveries significantly enhance the development of advanced materials and open new opportunities for engineering applications across aerospace, energy, electronics, and medical technologies.

6.2 Limitations and recommendations of the study

This study is limited to the calculation of structural, mechanical, and electronic properties at zero Kelvin, along with the effects of pressure using standard density functional theory electronic structure methods. The study does not examine the behavior of $X_3\text{Ru}$ alloys under dynamic conditions such as elevated temperatures and stresses induced by rotation, which are more realistic for simulating their practical applications. Furthermore, the phase stability of $X_3\text{Ru}$ alloys at elevated temperatures including Gibbs free energies, thermal expansion coefficients, thermal conductivity, oxidation, and corrosion properties has not been addressed here and will be explored in future research. As artificial intelligence becomes increasingly integrated into scientific studies, we recommend employing additional resources such as machine learning as an alternative approach to identify promising materials, which can then be investigated further using first-principles methods. Finally, all the calculations presented in this study are purely computational, with no accompanying experimental validation, leaving an important gap that remains to be addressed.

Appendix

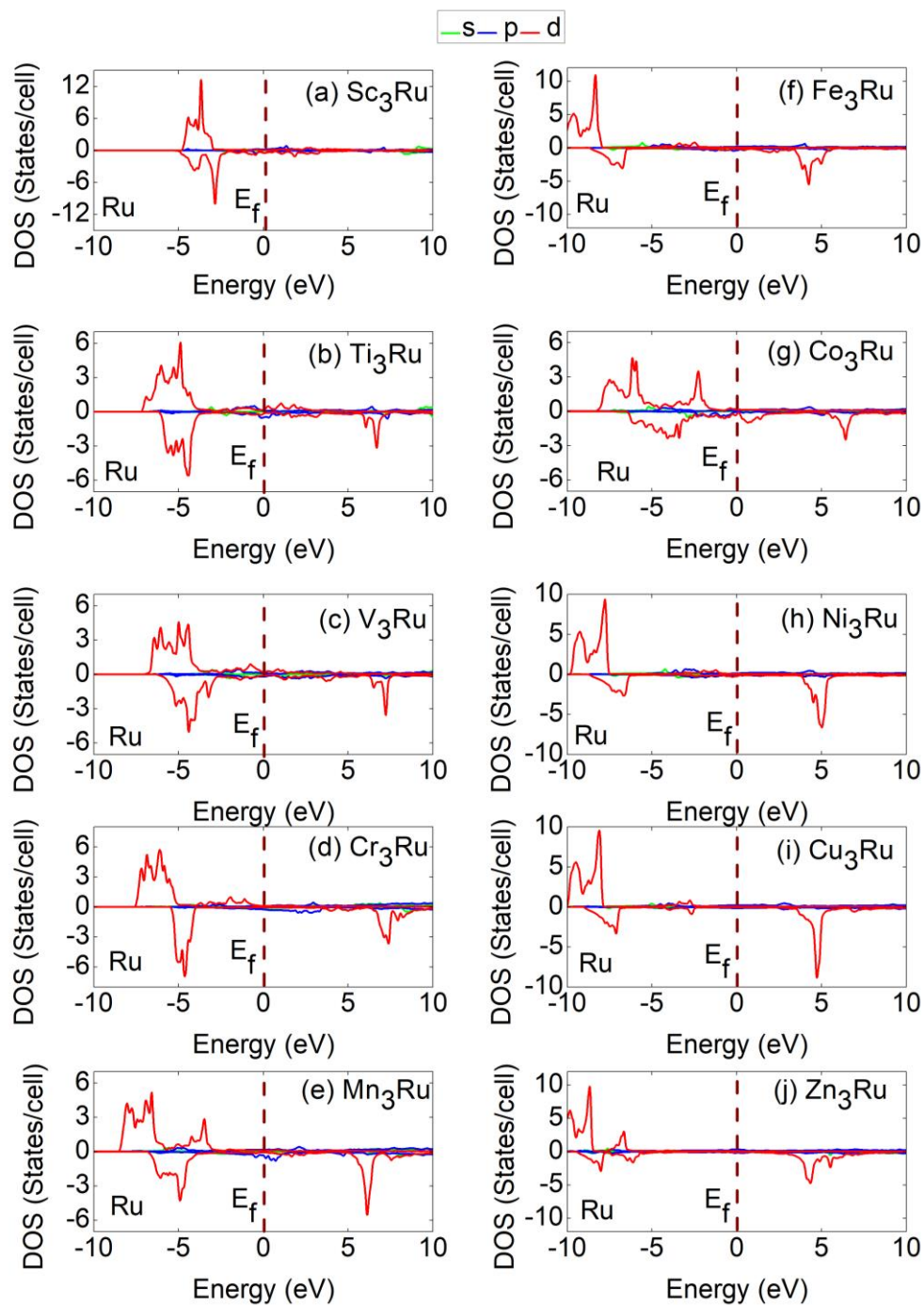


Figure 4.11: The spin-polarized partial density of states (PDOS) of Ru in all A15-type 3d- X_3 Ru transition compounds ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) was calculated using the GGA functional. The Fermi energy for each compound is set to zero. Additionally, the y-axis of the Ru PDOS has been magnified to better visualize the contributions from the deep s, p, and d states.

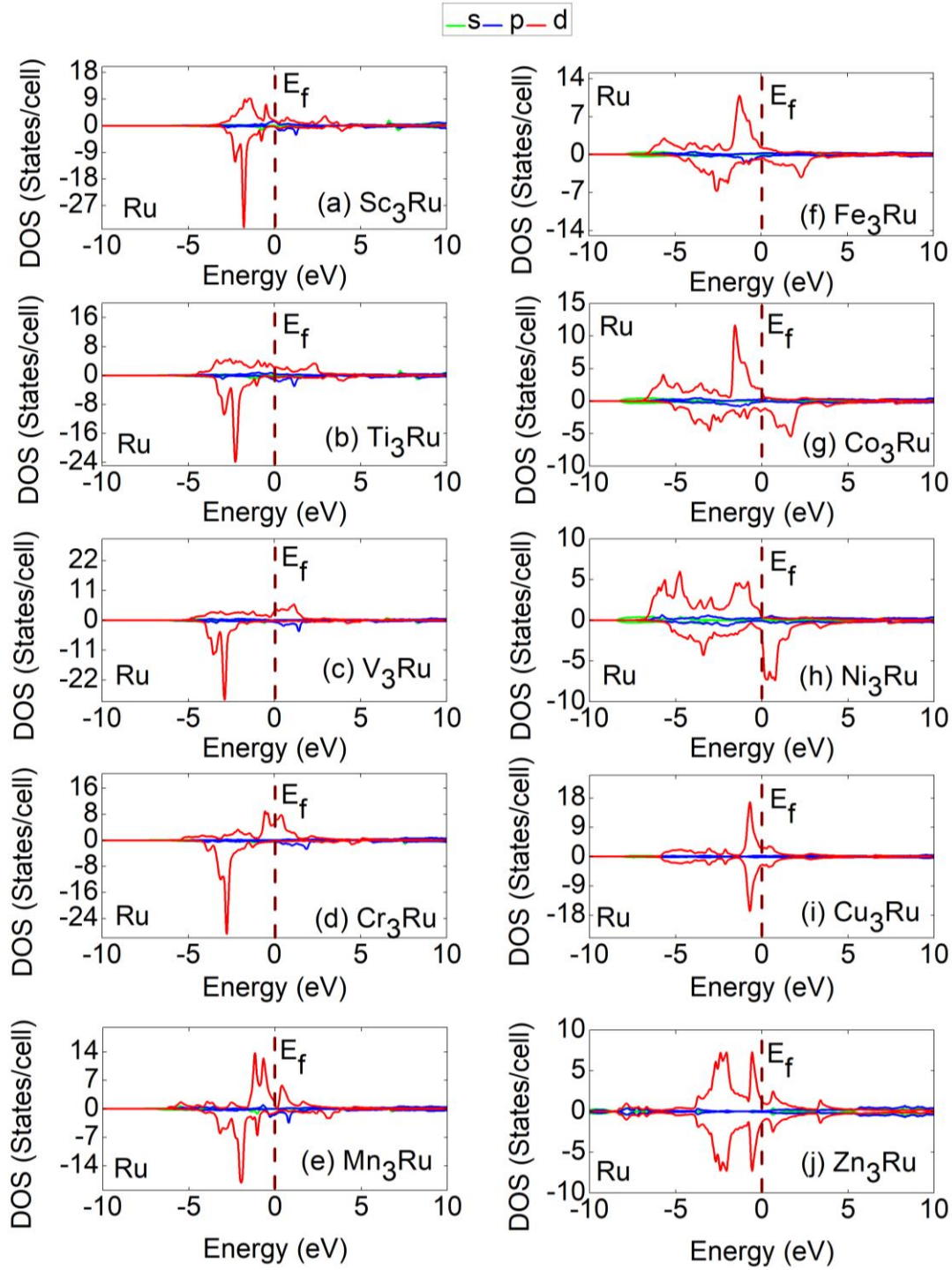


Figure 4.12: The spin-polarized partial density of states (PDOS) of Ru in all D0c-type 3d- X_3 Ru transition compounds ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) were calculated using the GGA functional. The Fermi energy for each compound is set to zero. Additionally, the y-axis of the Ru PDOS has been magnified to better visualize the contributions from the deep s, p, and d states.

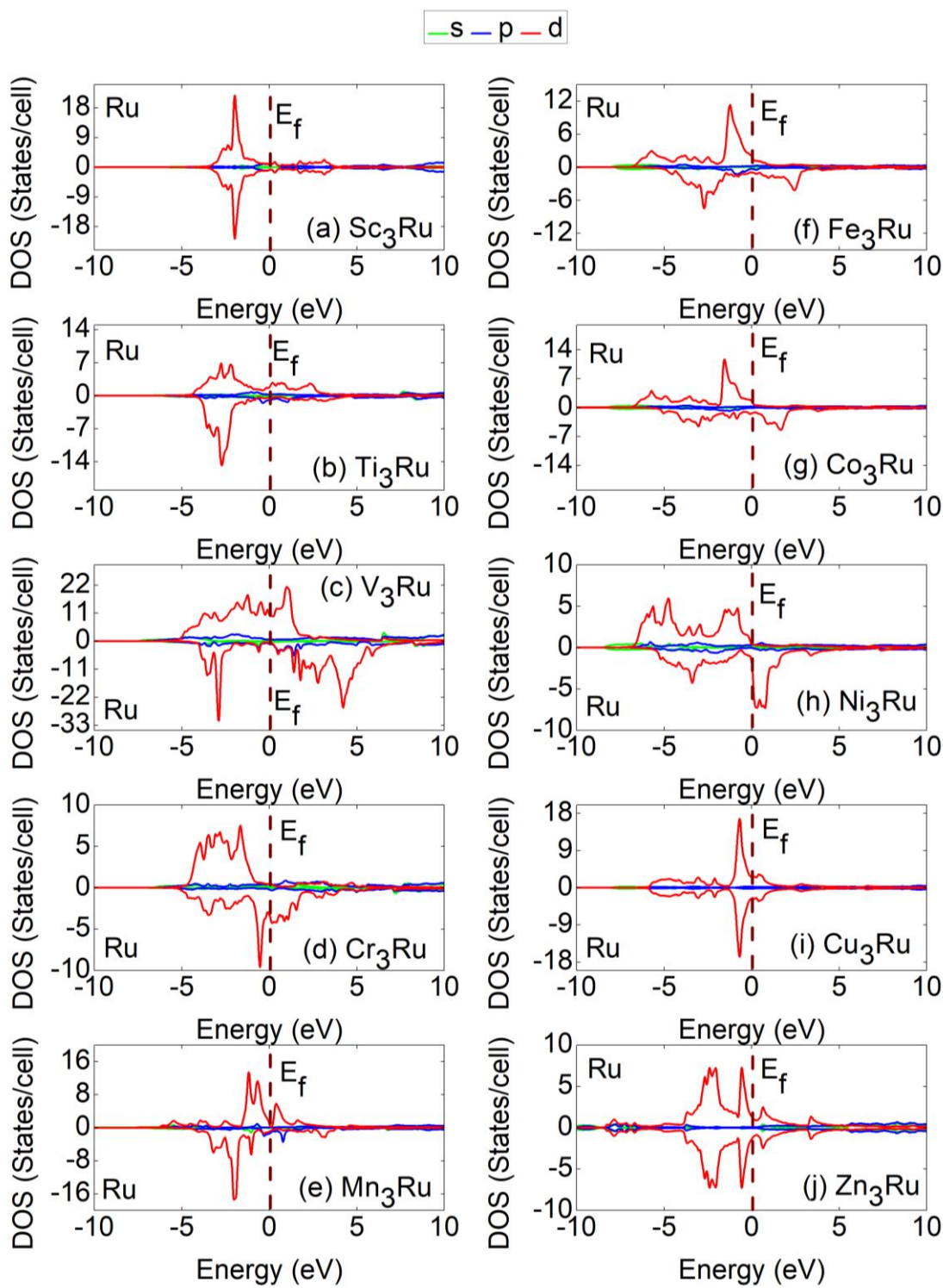


Figure 4.13: The spin-polarized partial density of states (PDOS) of Ru in all tP16-type 3d- X_3 Ru transition compounds ($X = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn}$) was calculated using the GGA functional. The Fermi energy for each compound is set to zero. Additionally, the y-axis of the Ru PDOS has been magnified to better visualize the contributions from the deep s, p, and d states.

Table 5.20: Summary of the computational parameters used in this study for A15, D0c and tP16 X₃Ru (X = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) alloys

Parameters	Value/Setting	Reason
Exchange–correlation functional	Generalized gradient approximation +Hubbard U (GGA+U= 2.5 eV)	For accurate on-site description of correlated 3d-transition metals.
Pseudopotentials	Ultrasoft-pseudopotential	For accurate treatment of core–valence interactions
Plane–wave cutoff energy	800 eV for all phases	Converged with an accuracy of 0.01 eV
k-point mesh	15 × 15 × 15 for A15, 15 × 15 × 10 for D0c and 15 × 15 × 11 for tP16 phases	Fully converged with the accuracy of 0.001 eV.
Electronic convergence criterion on energy, forces, atomic displacement and stress.	5.0 × 10 ⁻⁶ eV per atom for all phases, 0.01 eV Å ⁻¹ , 0.0005 Å, and 0.02 GPa.	Ensures reliable and accurate total energy calculations
interpolation integration method	Set to “Fine”.	For accurate calculation of density of states (DOS)
Spin polarization	Enabled	Accounts for magnetic contributions
Software package	CASTEP 2020	Version used for reproducibility
Smearing width	Set to 0.001 eV	Accurate for metallic systems

References

- [1] Shi J, Bai T, Zhao Z, Tan H, Driving economic growth through transportation infrastructure: An in-depth spatial econometric analysis., *Sustainability* 16 (2024) 4283.
- [2] Jili F, Gumede S, Goebel J, Wilson J, Assessing Transport Affordability and Spatial Inequality: Evidence from a Hierarchical Bayesian Regression Framework of South Africa's Provinces., *Urban Sci.* 10 (2026) 117.
- [3] Han X, Cao Y, Qu D, Feng W, Ma Y, A gas turbine performance mitigation control method based on state assessment., *Reliab. Eng. Syst. Saf.* 275 (2026) 112874.
- [4] Chengjie L I, Bin Y U, Chan H A, Yongbin J I, Yuxuan W A N, Xiaoran L U O, Zhichao C H E N, Yu Z H A O, Jiang Q I N, Energy and power transition in green aviation: Current status and prospects of synergistic development of alternative fuels and propulsion technologies., *Chin. J. Aeronaut.* (2026) 1–61.
- [5] N. Rao, N. Kumar, B. Prasad, N. Madhulata, N. Gurajrapu, Failure mechanisms in turbine blades of a gas turbine Engine—An overview, *Int J Eng Res Dev* 10 (2014) 48–57.
- [6] B.L. Koff, Gas turbine technology evolution: A designers perspective, *J. Propuls. Power* 20 (2004) 577–595.
- [7] R. Saniz, L.-H. Ye, T. Shishidou, A.J. Freeman, Structural, electronic, and optical properties of NiAl 3: first-principles calculations, *Phys. Rev. B* 74 (2006) 14209.
- [8] C.T. Sims, N.S. Stoloff, W.C. Hagel, *superalloys II*, Wiley New York, 1987.
- [9] T. Suzuki, Y. Oya, S. Ochiai, The mechanical behavior of nonstoichiometric compounds Ni 3 Si, Ni 3 Ge, and Fe 3 Ga, *Metall. Trans. A* 15 (1984) 173–181.
- [10] D.-M. Wee, T. Suzuki, The temperature dependence of hardness of L12 ordered alloys, *Trans. Jpn. Inst. Met.* 20 (1979) 634–646.
- [11] L.A. Cornish, B. Fischer, R. Völkl, Development of platinum-group-metal superalloys for high-temperature use, *MRS Bull.* 28 (2003) 632–638.
- [12] C. Huang, Y. Yamabe-Mitarai, H. Harada, The stabilization of Pt3Al phase with L12 structure in Pt–Al–Ir–Nb and Pt–Al–Nb alloys, *J. Alloys Compd.* 366 (2004) 217–221.
- [13] C. Huang, Y. Yamabe-Mitarai, K. Nishida, H. Harada, Phase constituents of Ir–Nb–Pt–Al quaternary alloys, *Intermetallics* 11 (2003) 917–926.
- [14] Sims C T, Stoloff N S, Hagel W C, *Superalloys II*, Wiley New York, 1987.
- [15] Gogia A.K, High-temperature Titanium Alloys, *Def. Sci. J.* 55 (2005) 149–173.
- [16] Bania P J, Parris W M, Beta-21s: a high temperature metastable beta titanium alloy., *Titan. Prod Appl Proc Tech Program Int Conf 2* (1990) 784–793.
- [17] P.J. Loferski, *Minerals Yearbook—Platinum Group Metals*, US Geol. Surv. Wash. DC (2008).
- [18] P. Caron, High γ 'solvus new generation nickel-based superalloys for single crystal turbine blade applications, *Superalloys 2000* (2000) 737–746.
- [19] D.R. Lide, *CRC handbook of chemistry and physics*, CRC Boca Raton, 2012.
- [20] B.O. Mnisi, E.M. Benecha, H.R. Chauke, P.E. Ngoepe, M.M. Tibane, Effect of transition metal doping on Cr–Ru alloys using first principles approach, *Bull. Mater. Sci.* 43 (2020) 1–9.
- [21] Dey G K, Sekhar J A, Micropyretic synthesis of tough NiAl alloys, *Metall. Mater. Trans. B* 28 (1997) 905–918.
- [22] Aoki K, Izumi O, Ductility and fracture behavior of B-doped polycrystalline Ni3Al, *J Jpn Inst Met* 43 (1979) 1190–1194.
- [23] Aoki K, Izumi O, Flow and fracture behaviour of Ni3 (Al· Ti) single crystals tested in tension, *J Mater Sci* 14 (1979) 1800–1806.
- [24] Koff B L, Gas turbine technology evolution: A designers perspective, *J Propuls Power* 20 (2004) 577–595.

- [25] Esgar J B, Reynolds R A, High temperature turbines. AGARD., 1971.
- [26] Clifton D, Tarassenko L, Condition monitoring of gas-turbine engines, of Oxford, Department of Engineering Science, 2006.
- [27] Reed R C, The Superalloys: Fundamentals and Applications., Cambridge University Press, 2006.
- [28] Papamoschou D, Engine cycle and exhaust configuration for quiet supersonic propulsion, *J Propuls Power* 20 (2004) 255–262.
- [29] Meetham G W, High temperature materials in gas turbine engines, *Mater Des* 9 (1988) 213–219.
- [30] Gas turbine engineering handbook, Fourth edition, Elsevier, The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK, 2011.
- [31] DeMasi-Marcin J T, Gupta D K, Protective coatings in the gas turbine engine, *Surf Coat Technol* 68 (1994) 1–9.
- [32] Harman, R.T, Harman, R.T., Applications for gas turbine engines., *Gas Turbine Eng. Appl. Cycles Charact.* (1981) 18–33.
- [33] Mnisi B O, First principles study of structural, electronic and mechanical properties of ternary Ru-Cr-X alloys, MSc Thesis, University of South Africa, 2017.
- [34] Süss R, Cornish L A, Glatzel U, Comparison of experimentally determined and CALPHAD-determined results of the Pt-Cr-Ru System, *CALPHAD XXXIII Program Abstr.* 34 (2004).
- [35] Segersäll M, Nickel-Based Single-Crystal Superalloys-the crystal orientation influence on high temperature properties, PhD Thesis, Linkopings Universitet, 2013.
- [36] Saniz R, Ye L H, Shishidou T, Freeman A .J, Structural, electronic, and optical properties of NiAl 3: first-principles calculations, *Phys. Rev. B—Condensed Matter Mater. Phys.* 74 (2006) 014209.
- [37] Xu J H, Min B I, Freeman A .J, Oguchi T, Phase stability and magnetism of Ni₃Al, 41 (1990) 1–7.
- [38] Sigfusson T I, Bernhoeft N R, Lonzarich G G, Magnetocrystalline anisotropy and Fermi surface of Ni₃Al, *J. Appl. Phys.* 53 (1982) 8207–8209.
- [39] Dood De, Chatel De F, Low temperature specific heat of Ni₃Al and Ni₃Ga, *J. Phys. F Met. Phys.* 3 (1973) 1039–1053.
- [40] Xu J.H, Oguchi T, Freeman A.J, Solid-solution strengthening: substitution of V in Ni₃Al and structural stability of Ni₃(Al, V), *Phys. Rev. B* 36 (1987) 4186.
- [41] Davis J R, ASM specialty handbook: heat-resistant materials, Asm International, 1997.
- [42] Wolff I M, Hill P J, Platinum metals-based intermetallics for high-temperature service, *Platin Met Rev* 44 (2000) 158–166.
- [43] Sharafat S, Kobayashi A, Chen Y, Ghoniem N M, Plasma spraying of micro-composite thermal barrier coatings, *Vacuum* 65 (2002) 415–425.
- [44] Yokokawa T, Osawa M, Nishida K, Kobayashi T, Koizumi Y, Harada H, Partitioning behavior of platinum group metals on the γ and γ' phases of Ni-base superalloys at high temperatures, *Scr Mater* 49 (2003) 1041–1046.
- [45] Vorberg S, Fischer B, Wenderoth M, Glatzel U, Völkl R, A TEM investigation of the γ/γ' phase boundary in Pt-based superalloys, *JOM* 57 (2005) 49–51.
- [46] Hill P J, Cornish L A, Fairbank G B, New developments in high-temperature platinum alloys, *JOM* 53 (2001) 19–20.
- [47] Yao B, Zhou X, Xiong D, Yu J, Liu M, Wang L, Phase stability, electronic structure and mechanical properties of Cr and Ti doped Pt₃Al: first-principles calculations., *Mater. Res. Express* 5 (2018) 1–7.
- [48] Popoola A I, Chown L H, Cornish L A, Theoretical investigations of Pt₃X (X = Al, Sc, Hf, Zr) ground state, *Turk. J. Phys.* 38 (2014) 1–8.
- [49] Hill P J, Yamabe-Mitarai Y, Wolff I M, High-temperature compression strengths of precipitation-strengthened ternary Pt-Al-X alloys, *Scr Mater* 44 (2001) 43–48.

- [50] Hüller M, Wenderoth M, Glatzel U, Völkl R, Vorberg S, Fischer B, Optimization of composition and heat treatment of age-hardened Pt-Al-Cr-Ni alloys, *Metall. Mater. Trans. A* 36 (2003) 681–689.
- [51] Cornish L A, Fischer B, Völkl R, Development of platinum-group-metal superalloys for high-temperature use, *MRS Bull* 28 (2003) 632–638.
- [52] Hill P J, Adams N, Biggs T, Hohls J, Taylor S S, Wolff I M, Platinum alloys based on Pt–Pt₃Al for ultra-high temperature use, *Mater. Sci. Eng. A* 329 (2002) 295–304.
- [53] A.I. Popoola, J.E. Lowther, Computational Study of Platinum Group Superalloys, *Int J Mod Phys B* 28 (2014) 1450066.
- [54] Zakharov P V, Korznikova E A, Dmitriev S V, Ekomasov E G, Zhou K, Surface discrete breathers in Pt₃Al intermetallic alloy, *Surf Sci* 679 (2019) 1–5.
- [55] Pan Y, Jin C, Mao P, Role of vacancies on electronic and elastic properties of RuAl₂ semiconducting compound from first-principles calculations, *J Electron Mater* 46 (2017) 6639–6645.
- [56] Alam M Z, Kamat S V, Jayaram V, Karamched P S, Ghosal P, Das D K, Dynamic recovery and recrystallization during high-temperature tensile deformation of a free-standing Pt-aluminide bond coat, *Mater. Sci. Eng. A* 604 (2014) 18–22.
- [57] Pan Y, Shi C S, Influence of alloying elements on the mechanical properties of PtAl₂ from first-principles calculations, *JOM* 70 (2018) 2463–2467.
- [58] Grushko B, Kapush D, Su J, Wan W, Hovmöller S, Al-rich region of Al–Pt, *J. Alloys Compd.* 580 (2013) 618–625.
- [59] Huang C, Yamabe-Mitarai Y, Harada H, The stabilization of Pt₃Al phase with L1₂ structure in Pt–Al–Ir–Nb and Pt–Al–Nb alloys, *J Alloys Compd* 366 (2004) 217–221.
- [60] Chauke H R, Minisini B, Drautz R, Nguyen-Manh D, Ngoepe P E, Pettifor D G, Theoretical investigation of the Pt₃Al ground state, *Intermetallics*, *Intermetallics* 18 (2010) 417–421.
- [61] Fischer B, New platinum materials for high temperature applications, *Adv Eng Mater* 3 (2001) 811–820.
- [62] Zhang X, He S, Peng G, Wei K, Wang X, Wang X, Feng J, Cai H, Chen L, Chen D, Wei Y, Strengthening mechanisms of platinum-iridium group alloys for ultra-high temperature applications: A review., *Int. J. Refract. Met. Hard Mater.* (2026) 107760.
- [63] Huang C, Yamabe-Mitarai Y, Nishida K, Harada H, Phase constituents of Ir–Nb–Pt–Al quaternary alloys, *Intermetallics* 11 (2003) 917–926.
- [64] Huang C, Nishida K, Yamabe-Mitarai Y, Harada H, Equilibrium phases at the Ir-rich corner of the Ir–Nb–Ni–Al quaternary system, *Intermetallics* 10 (2002) 893–902.
- [65] Cornish L A, Hohls J, Hill P J, Prins S, Süß R, Compton D N, The development of platinum-based alloys and their thermodynamic database., *J. Min. Metall. Sect. B Metall.* 38 (2002).
- [66] Wei Z, Xie Y, Xiao Y, Chen Z, Xue J, Qu N, Liu Y, Wu B, Zhu J, Rational analysis of atomic doping on the electronic structure and mechanical properties of Pt-based alloys., 40 (2025) 1605–1615.
- [67] Mnisi B O, Ali I O A, Benecha E M, Tibane M M, Phase stability and electronic properties of Cubic PtY, Pt₂Y, Pt₃Y, PtSc Pt₃Sc and orthorhombic PtY, PtY₂, PtY₃ PtSc₂ platinum-based alloys: A first principles DFT study, *Mater. Today Commun.* 51 (2026) 114921.
- [68] Gu Y, Yamabe-Mitarai Y, Ro Y, Yokokawa T, Harada H, Microstructures and compressive properties of Ir-15Nb refractory superalloy containing nickel, *Scr Mater* 39 (1998) 723–728.
- [69] Peng L M, Synthesis and mechanical properties of niobium aluminide-based composites, *Mater. Sci. Eng. A* 408 (2008) 232–236.
- [70] Lee K M, Lee J S, Lee D J, Kim S S, Ahn I S, Park M W, Effect of thermal treatment on the atomic ordering of mechanically alloyed Al₃Nb, *J Alloys Compd* 313 (2000) 214–217.
- [71] Jiao Z, Liu Q J, Liu F S, Wang W P, Wang W G, Li Y, Liu Z T, Electronic and mechanical properties of tetragonal Nb₂Al under high pressure: first-principles calculations., *Braz. J. Phys.* 46 (2016) 213–219.

- [72] Jiao Z, Li C, Bai Y, Zhang M J, Liu Q J, Ling X Y, Gong Y, Liu F S, Liu Z T, A comparative study of NbAl₃ and Nb₃Al intermetallic compounds under pressure., *Comput. Mater. Sci.* 126 (2017) 280–286.
- [73] Han L, Cao Z, Pan M, Hu Z, Huang Z, Wang J, Zhao Y, Deng D, The effect of antisite defects on the mechanical and dynamic stability of Nb₃Al. *Journal of Physics: J. Phys. Condens. Matter* 35 (2023) 435401.
- [74] Xu C, Chen D, Zhang X, Wang Q, Yu J, Wang S, Guo J, Fu H, Chen R, Lookman T, High temperature Nb-Si alloys using data science: optimization of fracture toughness and high-temperature strength., *Nat. Commun.* (2026).
- [75] Bewlay, B.P., Jackson, M.R, Zhao, J.C, Subramanian, P.R, Mendiratta, M.G., Lewandowski, J.J, Ultrahigh-temperature Nb-silicide-based composites., *Mrs Bull.* 28 (2003) 646–653.
- [76] Yeh J W, Chen S K, Lin S J, Gan J Y, Chin T S, Shun T T, Tsau C H, Chang S Y, Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, *Adv. Eng. Mater.* 6 (2004) 299–303.
- [77] Tsai M H, Yeh J W, High-entropy alloys: a critical review, *Mater Res Lett* 2 (2014) 107–123.
- [78] Senkov O N, Scott J M, Senkova S V, Meisenkothen F, Miracle D B, Woodward C F, Microstructure and elevated temperature properties of a refractory TaNbHfZrTi alloy, *J Mater Sci* 47 (2012) 4062–4074.
- [79] Senkov O N, Scott J M, Senkova S V, Miracle D B, Woodward C F, Microstructure and room temperature properties of a high-entropy TaNbHfZrTi alloy, *J Alloys Compd* 509 (2011) 6043–6048.
- [80] Senkov O N, Senkova S V, Woodward C F, Effect of aluminum on the microstructure and properties of two refractory high-entropy alloys, *Acta Mater* 68 (2014) 214–228.
- [81] Senkov O N, Wilks G B, Miracle D B, Chuang C P, Liaw P K, Refractory high-entropy alloys, *Intermetallics* 18 (2010) 1758–1765.
- [82] Senkov O N, Wilks G B, Scott J M, Miracle D B, Mechanical properties of Nb sub (25 Mo) sub (2) 5 Ta sub (25 W) sub (2) 5 and V sub (20 Nb) sub (2) 0 Mo sub (20 Ta) sub (2) 0 W sub (20 refractory high entropy alloys), *Intermetallics* 19 (2011) 698–706.
- [83] Xu Z Q, Ma Z L, Wang M, Chen Y W, Tan Y D, Cheng X W, Design of novel low-density refractory high entropy alloys for high-temperature applications, *Mater. Sci. Eng. A* 755 (2019) 318–322.
- [84] Ji J, Zhan S, Zhang Y, Review: Synthesis mechanism, microstructure, mechanical properties and oxidation behavior of refractory high-entropy alloys, *J. Mater. Sci.* (2026) 1–36.
- [85] Carpenter W J, George E P, Perspectives on refractory high-entropy alloys, *J. Mater. Res.* 40 (2025) 1887–1901.
- [86] Ghadami F, Davoudabadi M A, Entropy-driven design, microstructural evolution, and pathways to extreme-environment resilience., *J. Mater. Res. Technol.* 41 (2026) 2452–2466.
- [87] Peng S Y, Hsu T H, Yen H, Hsu W L, Yeh A C, Synergistic Control of Thermal Expansion and Oxidation Resistance in Novel Invar-Type Alloys., *Mater. Chem. Phys.* (2026) 132081.
- [88] Gomez-Gallegos A, Mandal P, Gonzalez D, Zuelli N, Blackwell P, Studies on titanium alloys for aerospace application., *Defect Diffus. Forum Trans Tech Publ. Ltd* 385 (2018) 419–423.
- [89] Braun J, Ellner M, Phase equilibria investigations on the aluminum-rich part of the binary system Ti-Al., *Metall. Mater. Trans. A* 32 (2001) 1037–1047.
- [90] Hussain A, Hayat S S, Choudhry M A, Ab-initio calculations of electronic structure and optical properties of TiAl alloy, *Phys. B Condens Matter* 406 (2011) 1961–1965.
- [91] Peters M, Kumpfert J, Ward C H, Leyens C, Titanium alloys for aerospace applications, *Adv. Eng. Mater.* 5 (2003) 419–427.
- [92] Boyer R R, An overview on the use of titanium in the aerospace industry, *Mater. Sci. Eng. A* 213 (1996) 103–114.

- [93] Das S, Anand S, Vishwakarma P S, Singh R, Mukherjee S K, Sinha S K, Kumar R, Shikha D, Kale A, Mahtre U, Ojha S, Formation of TiN protective layer at 500 C for enhanced oxidation resistance of IMI 834 titanium alloy in aerospace engine applications., *Ceram. Int.* 55 (2025) 53508–53518.
- [94] Yang N, Wang R, Shi L, Chen H, Yang H, Peng C, Zhang S, Deformation and Solution Treatment on Microstructure and Texture of IMI834 Plate., *Rare Met. Mater. Eng.* 55 (2026) 491–500.
- [95] Gu Y F, Harada H, Ro Y, Chromium and chromium-based alloys: Problems and possibilities for high-temperature service, *JOM* 56 (2004) 28–33.
- [96] Newkirk J W, Sago J A, ductile-phase toughening of cr 3 si with chromium, *MRS Online Proc. Libr.* 194 (1990) 183–189.
- [97] Dorcheh A S, Galetz M C, Challenges in Developing Oxidation-Resistant Chromium-Based Alloys for Applications Above 900°C, *JOM* 68 (2016) 2793–2802.
- [98] Ma K, Blackburn T, Magnussen J P, Kerbstadt M, Ferreirós P A, Pinomaa T, Hofer C, Hopkinson D G, Day S J, Bagot P A J, Moody M P, Galetz M C, Knowles A J, Chromium-based bcc-superalloys strengthened by iron supplements, *Acta Mater* 257 (2023) 119183.
- [99] Block F E, Good P C, Asai G, Electrodeposition of High-Purity Chromium, *J Electrochem Soc* 106 (1959) 1–5.
- [100] Matsumoto Y, Oki K, Tanaka M, Fujigami F, Harada Y, Morinaga M, Room-temperature ductility and surface notch sensitivity of chromium alloyed with vanadium and molybdenum, *Mater. Sci. Eng. A* 385 (2004) 133–139.
- [101] Reid C N, Gilbert A, Dislocation structure in chromium, chromium-rhenium, and chromium-iron alloys, *Journal Common Met.* 10 (1966) 77–90.
- [102] Stephens P J, Witzke W R, Alloy softening in group via metals alloyed with rhenium, *J. Common Met.* 23 (1971) 325–342.
- [103] Locq D, Caron P, Ramusat C, Mévrel R, Quaternary chromium-based alloys strengthened by Heusler phase precipitation, *Mater. Sci. Eng. A* 647 (2015) 322–332.
- [104] Royer L, Mathieu S, Liebaut C, Steinmetz P, Study of the microstructure and oxidation behavior of chromium base alloys strengthened by NiAl precipitates “In Materials Science Forum,” *Trans Tech Publ. Ltd* 595 (2008) 117–125.
- [105] Doğan O N, Song X, Palacio D, Gao M C, Coherent precipitation in a high-temperature Cr-Ni-Al-Ti Alloy, *J Mater Sci* 49 (2014) 805–810.
- [106] Calderon H A, Fine M E, Weertman J R, Coarsening and morphology of β' particles in Fe-Ni-Al-Mo ferritic alloys, *Metall. Trans. A* 19 (1988) 1135–1146.
- [107] Stallybrass C, Sauthoff G, Ferritic Fe-Al-Ni-Cr alloys with coherent precipitates for high-temperature applications, *Mater. Sci. Eng. A* 387–389 (2004) 985–990.
- [108] Knowles A J, Dye D, Dodds R J, Watson, A, Hardie C D, Humphry-Baker S A, Tungsten-based bcc-superalloys, *Appl Mater Today* 23 (2021) 101014.
- [109] Knowles A J, Jun T S, Bhowmik A, Jones N G, Britton T B, Giuliani F, Stone H J, Dye D, A new beta titanium alloy system reinforced with superlattice intermetallic precipitates, *Scr Mater* 140 (2017) 71–75.
- [110] Ulrich A S, Pfizenmaier P, Soleimani A, Glatzel U, Galetz M C, Strengthened Cr-Si-base alloys for high temperature applications, *Int J Refract Met. Hard Mater* 76 (2018) 72–81.
- [111] Kroll W I, Das duktile Chrom., *Z. Für Anorg. Allg. Chem.* 226 (1935) 23–32.
- [112] Cornish, L.A, Suss, R, Watson, A, Preußner, J, Prins, S.N, Wenderoth, M, Volkl, R, Glatzel, U., Building a database for the prediction of phases in Pt-based superalloys, *J. South Afr. Inst. Min. Metall.* 107 (2007) 713–724.
- [113] Shongwe M B, Witcomb M J, Cornish L A, Papo J M, TEM studies of Pt-Al-Cr-Ru Alloys, *J. South. Afr. Inst. Min. Metall.* 112 (2012) 551–558.
- [114] Cornish L A, Chown L H, Platinum-based alloys and coatings: materials for the future?, *Adv. Gas Turbines* (2011) 337–370.

- [115] Süss R, Cornish L A, Witcomb M J, Investigation of as-cast alloys in the Pt–Cr–Ru system, *J Alloys Compd* 416 (2006) 80–92.
- [116] Zhang X, Fu T, Cui K, Zhang Y, Shen F, Wang J, Yu L, Mao H, The protection, challenge, and prospect of anti-oxidation coating on the surface of niobium alloy, *Coatings* 11 (2021) 742.
- [117] Zhang X, Deng H, Xiao S, Zhang Z, Tang J, Deng L, Hu W, Diffusion of Co, Ru and Re in Ni-based superalloys: a first-principles study, *J Alloys Compd* 588 (2014) 163–169.
- [118] Naher M I, Parvin F, Islam A K M A, Naqib S H, Physical properties of niobium-based intermetallics (Nb₃B; B = Os, Pt, Au): a DFT-based ab-initio study, *Eur. Phys. J. B* 91 (2018) 289.
- [119] Muchiri P W, Mwalukuku V M, Korir K K, Amolo G O, Makau N W, Hardness characterization parameters of Niobium Carbide and Niobium Nitride: A first principles study, *Mater Chem Phys* 229 (2019) 489–494.
- [120] Miracle D B, Senkov O N, A critical review of high entropy alloys and related concepts, *Acta Mater* 122 (2017) 448–511.
- [121] Huang X, Rabe K M, Ackland G J, First-principles study of the structural energetics of PdTi and PtTi, *Phys Rev B* 67 (2003) 24101.
- [122] Gu Y F, Ro Y, Kobayashi T, Harada H, Microstructural evolution and mechanical properties of Cr–Ru alloys, *Metall. Mater. Trans. A* 36 (2005) 577–582.
- [123] Scruggs D M, Ductile chromium composition, 1965.
- [124] Johansen H, Asai G, Room-Temperature Ductile Chromium, *J Electrochem Soc* 101 (1954) 604–612.
- [125] Caron P, High γ ' solvus new generation nickel-based superalloys for single crystal turbine blade applications, *Superalloys 2000* (2000) 737–746.
- [126] Jahnátek M, Levy O, Hart G L W, Nelson L J, Chepulskii R V, Xue J, Curtarolo S, Ordered phases in ruthenium binary alloys from high-throughput first-principles calculations, *Phys Rev B* 84 (2011) 214110.
- [127] Liao, P. K, K. E. Spear, The B–Cr (boron-chromium) system, *Bull. Alloy Phase Diagr.* 7 (1986) 232–237.
- [128] Liao K P, Spear K E, Massalski T B, Binary alloy phase diagrams, ASM Int. Mater. Park Ohio 1 (1990) 557–559.
- [129] Zhang X, Fu T, Cui K, Zhang Y, Shen F, Wang J, Yu L, Mao H, The protection, challenge, and prospect of anti-oxidation coating on the surface of niobium alloy, *Coatings* 11 (2021) 742.
- [130] Zhang S, Li X, Zuo J, Qin J, Cheng K, Feng Y, Bao W, Research progress on active thermal protection for hypersonic vehicles, *Prog. Aerosp. Sci.* 119 (2020) 100646.
- [131] Massalski T B, Okamoto H, Subramanian P R, Kacprzak L, Binary Alloy Diagram, 2nd edition, ASM International, 1990.
- [132] Oya Y, Mishima Y, Suzuki T, L12 D0c martensitic transformation in Pt₃Al and Pt₃Ga, *Z Met.* 78 (1987) 485–490.
- [133] Hill P J, Cornish L A, Ellis P, Witcomb M J, The effects of Ti and Cr additions on the phase equilibria and properties of (Pt)/Pt₃Al alloys, *J Alloys Compd* 322 (2001) 166–175.
- [134] McAlister A J, Kahan D J, The Al–Pt (Aluminum-Platinum) system, *Bull. Alloy Phase Diagr.* 7 (1986) 47–51.
- [135] Chattopadhyay T, Schubert K, Kristallstruktur von Pt₃Ga (r) und einigen Phasen der Mischung Pt₃Al, *J. Common Met.* 41 (1975) 19–32.
- [136] Kimmel G, On the U₃Si (Doc) crystallographic type, *J. Common Met.* 59 (1978) 83–86.
- [137] Laughlin D E, Massalski T B, Construction of equilibrium phase diagrams: Some errors to be avoided, *Prog Mater Sci* 120 (2021) 100715.
- [138] Raub E, Mahler W, Alloys of chromium with platinum, iridium, rhodium, and ruthenium, *Z Met.* 46 (1955) 210–215.
- [139] Greenfield P, Beck P A, Intermediate phases in binary systems of certain transition elements, *JOM* 8 (1956) 265–276.

- [140] Savitskii E M, Terekhova V F, Birun N A, Equilibrium Diagram of the Chromium-Ruthenium System, Sb Nauchn Rab Inst Met. Akad 18 (1964) 170–174.
- [141] Shurin A K, Dmitrieva G P, Nauchn S B, Phase Diagram of the System Chromium-Ruthenium, Sb Nauchn Rab Inst Met. Akad 18 (1964) 170–174.
- [142] Wopersnow W, Raub C J, The Alloys of Ruthenium with Palladium and Chromium as well as with Some Other Transition Metals, Metall 33 (1979) 1261–1265.
- [143] Waterstrat R M, analysis of selected alloys in the systems Cr-Pd, Cr-Ru, V-Pd and Ta-Pt, J. Common Met. 80 (1981) 31–36.
- [144] Venkatraman M, Neumann J P, The Cr– Ru (chromium-ruthenium) system, J. Phase Equilibria 8 (1987) 109–112.
- [145] Chevalier P Y, Fischer E, CrRu (Chromium e Ruthenium). In: Franke P, Neuschütz D, editors. Binary systems. part 5: binary systems supplement 1, Springer Berlin Heidelberg, 2007.
- [146] Saunders N, Miodownik A P, CALPHAD (calculation of phase diagrams): a comprehensive guide, Elsevier, 1998.
- [147] Lukas H, Fries S G, Sundman B, Computational thermodynamics: The Calphad method, Camb. Univ. Press U. S. (2007) 1–324.
- [148] Zhu L L, Qi H Y, Jiang L, Jin Z P, Zhao J C, Experimental determination of the Ni–Cr–Ru phase diagram and thermodynamic reassessments of the Cr–Ru and Ni–Cr–Ru systems, Intermetallics 64 (2015) 86–95.
- [149] Zhengyan Zhu, Ying-Jie Zhang, Yiwen Li, Qing Li, Wen Duan, Hai-Hu Wen, Comparative studies on superconductivity in Cr₃Ru compounds with bcc and A15 structures, J Phys Condens Matter 34 ((2022) 1–11.
- [150] Tohyama T, Ohta Y, Shimizu M, Tight-binding calculations of the electronic structure and magnetic properties in ordered TPt₃ (T= Ti, V, Cr, Mn, Fe and Co) alloys, J. Phys. Condens. Matter 1 (1989) 1789–1798.
- [151] Sinha A K, Close-packed ordered AB₃ structures in ternary alloys of certain transition metals., Trans Met Soc AIME 245 (1969) 911–917.
- [152] Lin W, Xu J H, Freeman A J, Electronic structure, cohesive properties, and phase stability of Ni₃V, Co₃V, and Fe₃V, Phys. Rev. B 45 (1992) 10863.
- [153] Boer De, Boom R, Miedema A R, Enthalpies of formation of liquid and solid binary alloys based on 3d metals: II alloys of chromium and manganese., Phys. B C (1982) 18–41.
- [154] Oikawa K, Qin G W, Ikeshoji T, Kitakami O, Shimada Y, Ishida K, Fukamichi, K, Thermodynamic calculations of phase equilibria of Co–Cr–Pt ternary system and magnetically induced phase separation in the FCC and HCP phases., J. Magn. Magn. Mater. 236 (2001) 220–233.
- [155] Goto T, Effects of the atomic environment on the magnetic properties of Cr-Pt alloys., J. Phys. Soc. Jpn. 43 (1977) 1848–1853.
- [156] Pickart S J, Nathans R, Neutron diffraction investigation of Pt-based alloys of the first transition series., J. Appl. Phys. 34 (1963) 6483.
- [157] Crangle J, Some magnetic properties of platinum-rich Pt-Fe alloys., J. Phys. Radium 20 (1959) 435–437.
- [158] Kussmann A, Muller K, Raub E, Thermomagnetic measurements on alloys of the platinum-group metals with chromium., Z Met. 59 (1968) 859–863.
- [159] Phasha M, Ngobe B, Diale R, First Principles Investigation of Binary FCC Pt-Ru and Pt-Ir Alloys., in: Spring nature, Singapore, 2024: pp. 128–136.
- [160] Yamabe-Mitarai Y, Aoyagi T, Abe T, An investigation of phase separation in the Ir–Pt binary system., J. Alloys Compd. 484 (2009) 327–334.
- [161] Tripathi S N, Chandrasekharaiah M S, Thermodynamic properties of binary alloys of platinum metals II: Ir-Pt system, J. Common Met. 91 (1983).

- [162] M.M. Tibane, Phase stability study of Pt-Cr and Ru-Cr binary alloys, PhD Thesis, University of Limpopo, 2011.
- [163] Williams D E G, Jezierski A, Magnetic order in crystallographically ordered Pt_{4-y} (M_nxCr_{1-x})_y alloys., J. Magn. Magn. Mater. 59 (1986) 41–56.
- [164] Lu Z W, Klein B M, Chau H T, Comparison of theoretical and experimental magnetization densities of Ni, Pt 3 Cr, and Pd 3 Cr., Phys. Rev. B 58 (1998) 9252.
- [165] Szajek A, The Study of the Electronic Structure of CrPt₃ Alloy by the LMTO Method., Acta Phys. Pol. A 82 (1992) 967–974.
- [166] Oppeneer P M, Antonov V N, Calculated magneto-optical Kerr spectra of compounds (X= V, Cr, Mn, Fe and Co)., J. Phys. Condens. Matter 8 (1996) 5769–5780.
- [167] Mnisi, B.O, Benecha, E.M, Chauke, H.R, Ngoepe, P.E, Tibane, M.M, Effect of transition metal doping on Cr–Ru alloys using first principles approach., Bull. Mater. Sci. 43 (2020) 1–9.
- [168] Wang C P, Ren H, Liu H, Li L L, Yang S Y, Han J J, Lu Y, Guo Y H, Huang Y X, Liu X J, Experimental investigation and thermodynamic assessment of phase equilibria in the Cr–Re–Ru ternary system, Calphad 74 (2021) 102289.
- [169] Nishihara, Y, Yamaguchi, Y, Tokumoto, M, Takeda, K, Fukamichi, K, Superconductivity and magnetism of bcc Cr–Ru alloys, Phys. Rev. B 34 (1986) 3446.
- [170] Hong J, Kim S, Kim J, First-principles study on the d-band center of Pt alloyed with 3 d transition metals., J. Korean Phys. Soc. 83 (2023) 964–969.
- [171] La P, Wei Y, Lv R, Zhao Y, Yang Y, Effect of Mn element on microstructure and mechanical properties of bulk nanocrystalline Fe₃Al based materials prepared by aluminothermic reaction, Mater. Sci. Eng. A 527 (2010) 2313–2319.
- [172] Sun Z, Fan Z, Jin G, Xin C, The structural and optical properties of Mn/Fe-doped KDP crystals: a first-principles calculation., J. Electron. Mater. 53 (2024) 891–898.
- [173] Papadimitriou I, Utton C, Tsakiroopoulos P, Ab initio investigation of the intermetallics in the Nb–Sn binary system, Acta Mater 86 (2015) 23–33.
- [174] M Born, R Oppenheimer, ur quantentheorie der molekeln., Ann Phys 389 (1927) 457–484.
- [175] R M Martin, Electronic structure: basic theory and practical methods, Cambridge university press, 2004.
- [176] Hohenberg, P, Kohn, W., Inhomogeneous electron gas, Phys. Rev. 136 (1964) 864.
- [177] S Tosoni, C Tuma, J Sauer, B Civalieri, P Ugliengo, A comparison between plane wave and Gaussian-type orbital basis sets for hydrogen bonded systems: Formic acid as a test case, J Chem Phys 127 (2007) 154102.
- [178] Calais J L, Density-functional theory of atoms and molecules. rg parr and w. yang, oxford university press, new york, oxford, 1989. ix+ 333 pp. price£ 45.00., Int. J. Quantum Chem. 47 (1993) 101–101.
- [179] W Kohn, L J Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133.
- [180] Singh D, Planes Waves, Pseudopotentials and the LAPW, 1994.
- [181] Stefano Fabris, Stefano de Gironcoli, Stefano Baroni, Gianpaolo Vicario, Gabriele Balducci, Taming multiple valency with density functionals: A case study of defective ceria, Phys Rev B 71 (2005) 041102.
- [182] Schwarz K, Mohn P, Itinerant metamagnetism in YCo₂., J. Phys. F Met. Phys. 14 (1984) p.L129.
- [183] Zeller R, Spin-polarized dft calculations and magnetism, Comput. Nanosci. 39 (2006) 419–445.
- [184] H J Kulik, M Cococcioni, D A Scherlis, N Marzari, Density functional theory in transition-metal chemistry: A self-consistent Hubbard U approach, Phys Rev Lett 97 (2006) 103001.
- [185] B Sun, P Zhang, X G Zhao, First-principles local density approximation+ U and generalized gradient approximation+ U study of plutonium oxides, J Chem Phys 128 (2008) 84705.

- [186] E H Lieb, Two theorems on the Hubbard model, *Phys Rev Lett* 62 (1989) 1201.
- [187] Cococcioni M, The LDA+ U approach: a simple Hubbard correction for correlated ground states. *Correlated Electrons: Models Mater. Model. Simul.* 2 (2012) 1–40.
- [188] Stephens P J, Devlin F J, Chabalowski C F, Frisch M J, Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields., *J. Phys. Chem.* 98 (1994) 11623–11627.
- [189] J Heyd, G E Scuseria, Assessment and validation of a screened Coulomb hybrid density functional, *J. Chem. Phys.* 120 (2004) 7274–7280.
- [190] Clark S J, Robertson J, Screened exchange density functional applied to solids, *Phys. Rev. B—Condensed Matter Mater. Phys.* 82 (2010) 085208.
- [191] P R Levashov, G V Sin'ko, N A Smirnov, D V Minakov, O P Shemyakin, K V Khishchenko, Pseudopotential and full-electron DFT calculations of thermodynamic properties of electrons in metals and semiempirical equations of state, *J. Phys. Condens. Matter* 22 (2010) 505501.
- [192] F Jansen, *Introduction to Computational Chemistry*, John, Wiley and Sons, 2017.
- [193] Marques M A, Maitra N T, Nogueira F M, Gross E K, Rubio A, *Fundamentals of time-dependent density functional theory*, 2012.
- [194] Filippetti A, Bachelet G.B, *Pseudopotential method*, Elsevier, 2005.
- [195] D R Hamann, M Schluter, C Chiang, Norm conserving pseudopotentials, *Phys Rev Lett* 43 (1979) 1494.
- [196] D R Hamann, Optimized norm-conserving Vanderbilt pseudopotentials, *Phys Rev B Condens Matter Mater Phys* 58 (1998) 085117.
- [197] A.I. Popoola, *Computational study of noble metal alloys*, Thesis, Wits University, 2014.
- [198] K Laasonen, A Pasquarello, R Car, C Lee, D Vanderbilt, Car-Parrinello molecular dynamics with Vanderbilt ultrasoft pseudopotentials, *Phys Rev B* 47 (1993) 10142.
- [199] Vanderbilt D, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism., *Phys. Rev. B* 41 (1990) 7892.
- [200] G Kresse, J Hafner, R J Needs, Optimized norm-conserving pseudopotentials, *J. Phys. Condens. Matter* 4 (1992) 7451.
- [201] Sasaki T, Rappe A M, Louie S G, Ab initio optimized pseudopotential calculations of magnetic systems, *Phys Rev B* 52 (1995) p.12760.
- [202] Louie S G, Steven G, Sverre Froyen, Marvin L. Cohen, Nonlinear ionic pseudopotentials in spin-density-functional calculations, *Phys Rev B* 26 (1982) p.1738.
- [203] Cho J H, Scheffler M, Ab initio pseudopotential study of Fe, Co, and Ni employing the spin-polarized LAPW approach, *Phys Rev B* 53 (1996) p.10685.
- [204] Fabris S, de Gironcoli S, Baroni S, Vicario G, Balducci G, Reply to “Comment on ‘Taming multiple valency with density functionals: A case study of defective ceria’,” *Phys. Rev. B—Condensed Matter Mater. Phys.* 72 (2005) 237102.
- [205] Cottenier S, *Density Functional Theory and the family of (L) APW-methods: a step-by-step introduction.*, Inst. Voor Kern-En Stralingsfysica KU Leuven Belg. 4 (2002) 41.
- [206] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I.J. Probert, K. Refson, Mike C Payne, First principles methods using CASTEP, *Z. Krist.* 220 (2005) 567–570.
- [207] Segall MD, Lindan PJ, Probert MA, Pickard CJ, Hasnip PJ, Clark SJ, Payne MC, First-principles simulation: ideas, illustrations and the CASTEP code., *J. Phys. Condens. Matter* 14 (2002) 2717.
- [208] Cottenier S, *Density Functional Theory and the family of (L) APW-methods: a step-by-step introduction.*, Instituut voor Kern-en Stralingsfysica, KU Leuven, Belgium, 2002.
- [209] Schwarz K, Blaha P, Solid state calculations using WIEN2k, *Comput. Mater. Sci.* 28 (2003) pp.259-273.

- [210] Tosoni S, Tuma C, Sauer J, Civalleri B, Ugliengo P, A comparison between plane wave and Gaussian-type orbital basis sets for hydrogen bonded systems: Formic acid as a test case., *J. Chem. Phys.* 127 (2007) 154102.
- [211] Segall M D, An ab initio study of biological systems, PhD Thesis, University of Cambridge, 1997.
- [212] Kohanoff J, *Electronic structure calculations for solids and molecules: theory and computational methods.*, Cambridge University Press, UK, 2006.
- [213] Martin R M, *Electronic Structure: Basic theory and practical methods*, Cambridge University Press, UK, 2006.
- [214] E.M. Benecha, Theoretical study of magnetic ordering of defects in diamond, Doctoral dissertation, PhD Thesis, University of South Africa, 2011.
- [215] E B Lombardi, A quantum mechanical study of dopants in diamond, PhD Thesis, University of South Africa, 2002.
- [216] Blaha P, Schwarz K, Madsen G K, Kvasnicka D, Luitz J, *wien2k.*, Augment. Plane Wave Local Orbitals Program Calc. Cryst. Prop. 60 (2001).
- [217] C G Broyden, The convergence of a class of double-rank minimization algorithms: 2, *IMA J Appl Math* 6 (1970) 222–231.
- [218] R Fletcher, A new approach to variable metric algorithms, *Comput J* 13 (1970) 317–322.
- [219] D Goldfarb, A Family of Variable-Metric Methods Derived by Variational Means, *Mathematics Of Computation* 24 (1970) 23–26.
- [220] D F Shanno, Conditioning of quasi-Newton methods for function minimization, *Math Comput* 24 (1970) 647–656.
- [221] J M Rondinelli, B Deng, L D Marks, Enhancing structure relaxations for first-principles codes: An approximate Hessian approach, *Comput Mater Sci* 40 (2007) 345–353.
- [222] J Nocedal, S J Wright, *Numerical optimization*, Springer-Verlag New York, Inc, 1999.
- [223] Mattsson A E, Schultz P A, Desjarlais M P, Mattsson T R, Leung K, Designing meaningful density functional theory calculations in materials science—a primer., *Model. Simul. Mater. Sci. Eng.* 13 (2004) p.R1.
- [224] Monkhorst, H.J, Pack, J.D, Special points for Brillouin-zone integrations, *Phys. Rev. B* 13 (1976) 5188.
- [225] Joannopoulos J D, Cohen M L, Electronic charge densities for ZnS in the wurtzite and zincblende structures., *J. Phys. C Solid State Phys.* 15 (1973) 1572.
- [226] Chadi D J, Cohen M L, Special points in the Brillouin zone, *Phys Rev B* 8 (1973) 5747.
- [227] Material Studio, DS BIOVIA. Dassault System BIOVIA, 2000.
- [228] Payne M C, Teter M P, Allan D C, Arias T A, Joannopoulos A J, Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients., *Rev. Mod. Phys.* 64 (1992) 1045.
- [229] X Wu, F Kang, W Duan, J Li, Density functional theory calculations: A powerful tool to simulate and design high-performance energy storage and conversion materials, *Progress in Natural Science, Mater. Int.* 29 (2019) 247–255.
- [230] P Verma, D G Truhlar, Status and Challenges of Density Functional Theory, *Trends Chem* 2 (2020) 302–318.
- [231] N Mardirossian, M Head-Gordon, Thirty years of density functional theory in computational chemistry: An overview and extensive assessment of 200 density functionals, *Mol Phys* 115 (2017) 2315–2372.
- [232] Karl K Irikura, David J Frurip, *Computational Thermochemistry*, in: ACS Publications, 1998: pp. 2–18.
- [233] Li H, Shi L L, Zhang M, Su Z, Wang X J, Hu L H, Chen G H, Improving the accuracy of density-functional theory calculation:, *J Chem Phys* 126 (2007) 144101.

- [234] Mnisi, B.O, Benecha, E.M, Tibane, M.M, First-principles study on thermodynamic, structural, mechanical, electronic, and phonon properties of tP16 ru-based alloys, *Alloys* 3 (2024) 126–139.
- [235] B.O. Mnisi, E.M. Benecha, M.M. Tibane, Computational Study of A15 Ru-Based Alloys for High-Temperature Structural Applications, in: *Ruthenium - Elem. Loved Res.*, IntechOpen, 2021: p. 195.
- [236] Mnisi, B.O, Benecha, E.M, Tibane, M.M, Investigation of the thermodynamic, structural, electronic, mechanical and phonon properties of D0c Ru-based intermetallic alloys: An ab-initio Study, *Mater. Res. Express* 11 (2024) 046506.
- [237] L H Hu, X J Wang, L H Wong, G H Chen, Combined first-principles calculation and neural-network correction approach for heat of formation, *J. Chem. Phys.* 119 (2003) 11501–11507.
- [238] X Zheng, L H Hu, X J Wang, G H Chen, A generalized exchange-correlation functional: The Neural-Networks approach, *Chem Phys Lett* 390 (2004) 186–192.
- [239] N D M Hine, K Frensch, W M C Foulkes, M W Finnis, Supercell size scaling of density functional theory formation energies of charged defects, *Phys Rev B Condens Matter Mater Phys* 79 (2009) 024112.
- [240] O. N. Senkov, D. B. Miracle, Generalization of intrinsic ductile-to-brittle criteria by Pugh and Pettifor for materials with a cubic crystal structure, *Sci. Rep.* 11 (2021) 4531.
- [241] R.P. Thompson, W.J. Clegg, Predicting whether a material is ductile or brittle, *Curr. Opin. Solid State Mater. Sci.* 22 (2018) 100–108.
- [242] Perdew JP, Burke K, Ernzerhof M, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865.
- [243] J.P. Perdew, K. Burke, M. Ernzerhof, Perdew, burke, and ernzerhof reply, *Phys Rev Lett* 80 (1998) 891.
- [244] Mehl M.J, Papaconstantopoulos D.A, Applications of a tight-binding total-energy method for transition and noble metals: Elastic constants, vacancies, and surfaces of monatomic metals, *Phys. Rev. B* 54 (1996) 4519.
- [245] Hong S, Fu C.L, Phase stability and elastic moduli of Cr₂Nb by first-principles calculations, *Intermetallics* 7 (1999) 5–9.
- [246] Shiga M, Correlation between lattice constant and magnetic moment in 3d transition metal alloys., *AIP Conf. Proc.* 18 (1974) 463–477.
- [247] Osterwalder J, Correlation effects and magnetism in 3d transition metals, *J. Electron Spectrosc. Relat. Phenom.* 117 (2001) 71–88.
- [248] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys Rev B* 13 (1976) 5188.
- [249] Medvedeva N.I., Ivanovskii A.L, Ab-initio study of Re and Ru effect on stability of TCP nanoparticles in Ni-based superalloys, *Наносистемы Физика Химия Математика* 5 (2014) 486–493.
- [250] Mnisi, B.O, Benecha, E.M., Chauke, H.R, Ngoepe, P.E, Tibane, M.M, Effect of transition metal doping on Cr–Ru alloys using first principles approach, *Bull. Mater. Sci.* 43 (2020) 1–9.
- [251] Zhu Z, Zhang Y.J, Li Y, Li Q, Duan W, Wen H.H, Comparative studies on superconductivity in Cr₃Ru compounds with bcc and A15 structures, *J. Phys. Condens. Matter* 34 (2022) 475602.
- [252] Brown Ian G, *The Physics and Technology of Ion Sources*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004.
- [253] Kong F, Longo, R.C, Park M.S, Yoon J, Yeon D.H, Park J.H, Wang W.H, Santosh K.C, Doo S.G, Cho K, Ab initio study of doping effects on LiMnO₂ and Li₂MnO₃ cathode materials for Li-ion batteries., *J. Mater. Chem. A* 3 (2015) 8489–8500.

- [254] Krajci M, Hafner J, Covalent bonding and bandgap formation in intermetallic compounds: a case study for Al_3V , *J. Phys. Condens. Matter* 14 (2002) 1865.
- [255] Xu J.H, Freeman A.J, Bandfilling and structural stability of trialuminides: YAl_3 , ZrAl_3 , and NbAl_3 , *J. Mater. Res.* 6 (1991) 1188–1199.
- [256] Hong T, Watson-Yang T.J, Guo X.Q, Freeman A.J, Oguchi T, Xu J.H, Crystal structure, phase stability, and electronic structure of Ti-Al intermetallics: Ti_3Al , *Phys. Rev. B* 43 (1991) 1940.
- [257] Cheong B.H, Chang K.J, First-principles study of the structural properties of Sn under pressure., *Phys. Rev. B* 44 (1991) 4103.
- [258] Song Y, Guo Z.X, Yang R, Li D, First principles study of site substitution of ternary elements in NiAl , *Acta Mater.* 49 (2001) 1647–1654.
- [259] Heid R, Bohnen K.P, Renker B, Wolf T, Schober H, Ab initio lattice dynamics and electron-phonon coupling in the refractory compounds ZrN and HfN , *Phys. Rev. B—Condensed Matter Mater. Phys.* 71 (2005) 092302.
- [260] Ding W.J, Yi J.X, Chen P, Li D.L, Peng L.M, Tang B.Y, Elastic properties and electronic structures of typical Al–Ce structures from first-principles calculations, *Solid State Sci.* 14 (2012) 555–561.
- [261] Liu X, Feng Q, Tang B, Zheng J, Zheng Z, Zhou W, Tian J, Wang J, First-principles calculations of mechanical and thermodynamic properties of tetragonal Be_{12}Ti . *RSC advances*, *RSC Adv.* 9 (2019) 5302–5312.
- [262] Born, M, n the stability of crystal lattices. I. In *Mathematical Proceedings of the Cambridge Philosophical Society*, *Proc. Camb. Philos. Soc.* 36 (1940) 160–172.
- [263] Born M, Huang K, *Theory of Crystal Lattices*, 1956.
- [264] Sin'ko G.V, Smirnov N.A, Ab initio calculations of elastic constants and thermodynamic properties of bcc, fcc, and hcp Al crystals under pressure, *J. Phys. Condens. Matter* 14 (2002) 6989.
- [265] Gao, X, Jiang Y, Zhou R, Feng J, Stability and elastic properties of Y–C binary compounds investigated by first principles calculations., *J. Alloys Compd.* 587 (2014) 819–826.
- [266] Grimvall G, *Thermophysical properties of materials*, Elsevier, 1999.
- [267] Li X, Chen D, Wu Y, Wang M, Ma N, Wang H, Assessment on the structural, elastic and electronic properties of Nb_3Ir and Nb_3Pt : A first-principles study., *AIP Adv.* 7 (2017) 065012.
- [268] Naher M.I, Afzal M.A, Naqib S.H, A comprehensive DFT based insights into the physical properties of tetragonal superconducting Mo_5PB_2 , *Results Phys.* 28 (2021) 104612.
- [269] Naher M.I, Naqib S.H, An ab-initio study on structural, elastic, electronic, bonding, thermal, and optical properties of topological Weyl semimetal Ta X ($\text{X} = \text{P, As}$), *Sci. Rep.* 11 (2021) 5592.
- [270] Roknuzzaman M, Hadi M.A., Abden M.J, Nasir M.T, Islam A.K.M.A, Ali M.S, Ostrikov K, Naqib S.H, Physical properties of predicted Ti_2CdN versus existing Ti_2CdC MAX phase: An ab initio study, *Comput. Mater. Sci.* 113 (2016) 148–153.
- [271] Hill R, The elastic behaviour of a crystalline aggregate., *Proc. Phys. Soc. Sect. A* 65 (1952) 349.
- [272] Reuss A. J, Calculation of the flow limits of mixed crystals on the basis of the plasticity of monocrystals, *Z Angew Math Mech* 9 (1929) 49–58.
- [273] Luan X, Qin H, Liu F, Dai Z, Yi Y, Li Q, The mechanical properties and elastic anisotropies of cubic Ni_3Al from first principles calculations., *Crystals* 8 (2018) 307.
- [274] Falk F, Model free energy, mechanics, and thermodynamics of shape memory alloys., *Acta Metall.* 28 (1980) 1773–1780.
- [275] Prikhodko S.V, Yang H, Ardell A.J, Carnes J.D, Isaak D.G, Temperature and composition dependence of the elastic constants of Ni_3Al , *Metall. Mater. Trans. A* 30 (1999) 2403–2408.

- [276] McNaught, A.D, Compendium of chemical terminology, Oxf. Blackwell Sci. 1669 (1997) 464.
- [277] Salje, E, Phase transitions in ferroelastic and co-elastic crystals, *Ferroelectrics* 104 (1990) 111–120.
- [278] Pugh, S.F, Relations between the elastic moduli and the plastic properties of polycrystalline pure metals., *Lond. Edinb. Dublin Philos. Mag. J. Sci.* 45 (1954) 823–843.
- [279] Mnisi, B.O, Benecha, E.M, Tibane, M.M, Density functional theory studies of structural, electronic and optical properties of cubic 3d-transition metal nitrides, *Intermetallics* 137 (2021) 107272.
- [280] Mnisi, B.O, Ab initio study of phase stability and optical properties of TiN and VN nitrides in different phases., *Solid State Commun.* 377 (2024) 115390.
- [281] Mnisi, B.O, Density functional theory study of electronic and optical properties of ScN nitride in NaCl-B1, CsCl-B2, ZB-B3 and NiAs-B8 phases., *Bull. Mater. Sci.* 45 (2022) 16.
- [282] Mnisi, B.O, Benecha, E.M, Tibane, M.M, First-principles study of stability and electronic properties of B2 X–Ru alloys for high-temperature structural applications., *Mater. Adv.* 5 (2024) 5632–5643.
- [283] Mnisi, B.O, Tibane, M.M, ZrN doped with 3d transition metals: a computational investigation of main physical properties for high-temperature structural applications., *Mater. Res. Express* 11 (2024) 056514.
- [284] Uğur Yorulmaz, Ayberk Özden, Nihan K Perkgöz, Feridun Ay, Cem Sevik, Vibrational and mechanical properties of single layer MXene structures: a first-principles investigation, *Nanotechnology* 27 (2016) 335702.
- [285] Chen Li, Xudong Zhang, Feng Wang, Influence of TM elements on the mechanical and thermodynamic properties of Hf2Si intermetallics, *Vacuum* 220 (2024) 112793.
- [286] Wang, K, Zhang, X, Wang, F, Exploring the electronic, mechanical, anisotropic and optical properties of the Sc-Al-C MAX phases from a first principles calculations., *Chem. Phys. Lett.* 836 (2024) 141024.
- [287] Cheng, X-Y, Chen, X. Q, Li, D. Z, Li, Y. Y., Computational materials discovery: the case of the W–B system, *Acta Crystallogr. Sect. C Struct. Chem.* 70 (2014) 85–103.
- [288] Mnisi, B.O, Density functional theory study of structural, mechanical, electronic and optical properties of MoAlX (X= B, C, N and O) compounds., *Mater. Res. Express* 8 (2021) 096533.
- [289] Chowdhury, T, Rano, B.U.R, Syed, I.M, Naqib, S.H., 2024, A Detailed First-Principles Study of the Structural, Elastic, Thermomechanical, and Optoelectronic Properties of Binary Rare-Earth Tritelluride NdTe3., *Adv. Theory Simul.* 7 (2024) 2400528.
- [290] Ming-Min Zhong, Cheng Huang, Chun-Ling Tian, The structural stabilities, mechanical properties and hardness of chromium tetraboride: Compared with low-B borides, *Int. J. Mod. Phys. B* 30 (2016) 16.
- [291] Ming Tian, Xudong Zhang, Feng Wang, Structural, mechanical, electronic and thermodynamic properties of YBC, YB2C, YB2C2, Y2B3C2 intermetallics, *Mater. Today Commun.* 39 (2024) 108696.
- [292] Zerarga, F, Allali, D, Bouhemadou, A, Khenata, R, Deghfel, B, Essaoud, S.S, Ahmed, R, Al-Douri, Y, Safaai, S.S, Bin-Omran, S, Naqib, S.H, Ab initio study of the pressure dependence of mechanical and thermodynamic properties of GeB2O4 (B= Mg, Zn and Cd) spinel crystals., *Comput. Condens. Matter* 32 (2022) 00705.
- [293] Naher, M.I, Naqib, S.H, An ab-initio study on structural, elastic, electronic, bonding, thermal, and optical properties of topological Weyl semimetal Ta X (X= P, As)., *Sci. Rep.* 11 (2021) 5592.
- [294] D.G. Pettifor, Theoretical predictions of structure and related properties of intermettallics, *Mater. Sci. Technol.* 8 (1992) 345–349.

- [295] Frantsevich, Ivan Nikitich, Elastic constants and elastic moduli of metals and insulators., 1982.
- [296] Greaves, George Neville, A. Lindsay Greer, Roderic S. Lakes, Tanguy Rouxel, Poisson's ratio and modern materials, *Nat. Mater.* 10 (2011) 823–837.
- [297] Thompson R. P, Clegg W. P, Predicting whether a material is ductile or brittle, *Curr. Opin. Solid State Mater. Sci.* 22 (2018) 100–108.
- [298] Huang C, Chen L, Negative Poisson's ratio in modern functional materials, *Adv. Mater.* 28 (2016) 8079–8096.
- [299] Mott P. H, Roland C. M, Limits to Poisson's ratio in isotropic materials, *Phys. Rev. B—Condensed Matter Mater. Phys.* 80 (2009) 132104.
- [300] Norris A.N, Poisson's ratio in cubic materials, *Proc. R. Soc. Math. Phys. Eng. Sci.* 462 (2006) 3385–3405.
- [301] Köster W, Franz H, Poisson's ratio for metals and alloys, *Metall. Rev.* 6 (1961) 1–56.
- [302] Wojciechowski K W, Poisson's ratio of anisotropic systems, *Comput Methods Sci Technol* 11 (2005) 73–79.
- [303] Tian, Y, Xu, B, Zhao, Z, Microscopic theory of hardness and design of novel superhard crystals, *Int. J. Refract. Met. Hard Mater.* 33 (2012) 93–106.
- [304] Vepřek S, Nanostructured Superhard Materials. In: Riedel R, editor. *Handbook of ceramic hard materials*. Weinheim:, Wiley-VCH, 2000.
- [305] Haines J, Leger JM, Bocquillon G, Synthesis and design of superhard materials, *Annu Rev Mater Res* 31 (2001) 1–23.
- [306] Gilman JJ., *Chemistry and physics of mechanical hardness.*, Hoboken, NJ: Wiley, 2009.
- [307] Solozhenko VL, Gregoryanz E, Synthesis of superhard materials, *Mater Today* 8 (2005) 44–51.
- [308] Sung CM, Sung M, Carbon nitride and other speculative superhard materials, *Mater Chem Phys* 43 (1996) 1–18.
- [309] Gu, Q, Krauss, G, Steurer, W, The generalized Lindemann melting coefficient, *Adv. Mater.* 20 (2008) 3620–3626.
- [310] Synthesis of ultra-incompressible superhard rhenium diboride at ambient pressure, *Science* 316 (2007) 436–9.
- [311] Crowhurst JC, Goncharov AF, Sadigh B, Evans CL, Morrall PG, Ferreira JL, et al, Synthesis and characterization of the nitrides of platinum and iridium., *Science* 311 (2006) 1275–8.
- [312] Cumberland RW, Weinberger MB, Gilman JJ, Clark SM, Tolbert SH, Kaner RB, an ultra-incompressible, hard material., *J Am Chem Soc* 127 (2005) 7264–5.
- [313] Zhao Y, He DW, Daemen LL, Shen TD, Schwarz RB, Zhu Y, et al, Superhard B-C-N materials synthesized in nanostructured bulks, *J Mater Res* 17 (2002) 3139–3145.
- [314] Solozhenko VL, Andrault D, Fiquet G, Mezouar M, Rubie DC, Synthesis of super hard cubic BC₂N, *Appl Phys Lett* 78 (2001) 1385–1387.
- [315] Solozhenko VL, Kurakevych OO, Andrault D, Le Godec Y, Mezouar M., Ultimate metastable solubility of boron in diamond: synthesis of superhard diamondlike BC₅, *Phys. Rev. Lett.* 102 (2009) 102:015506.
- [316] Solozhenko VL, Kurakevych OO, Oganov AR, On the hardness of a new boron phase, orthorhombic gamma-B-28, *J Superhard Mater* 30 (2008) 428–9.
- [317] Xiaohong Li, Hongling Cui, Ruizhou Zhang, First-principles study of the electronic and optical properties of a new metallic MoAlB, *Sci. Rep.* 6 (2016) 39790.
- [318] Brahma Raju Golla, Amartya Mukhopadhyay, Bikramjit Basu, Sravan Kumar Thimmappa, Review on ultra-high temperature boride ceramics, *Prog. Mater. Sci.* 111 (2020) 100651.
- [319] Li Q, Wang H, Ma YM, Predicting new superhard phases., *J Superhard Mater* 32 (2010) 192–204.
- [320] Chen, X.Q, Niu, H, Li, D, Li, Y, Modeling hardness of polycrystalline materials and bulk metallic glasses, *Intermetallics* 19 (2011) 1275–1281.

- [321] Xinghe Luan, Hongbo Qin, Fengmei Liu, Zongbei Dai, Yaoyong Yi, Qi Li, The Mechanical Properties and Elastic Anisotropies of Cubic Ni₃Al from First Principles Calculations, *Crystals* 8 (2018) 2–11.
- [322] Ranganathan S. I, Ostoja-Starzewski M, Universal elastic anisotropy index, *Phys. Rev. Lett.* 101 (2008) 055504.
- [323] Zener C, Elasticity and anelasticity of metals, Univ. Chic. Press (1965).
- [324] Chung, D.H., Buessem, W.R, The voigt-reuss-hill approximation and elastic moduli of polycrystalline MgO, CaF₂, β -ZnS, ZnSe, and CdTe., *J. Appl. Phys.* 38 (1967) 2535–2540.
- [325] W.Hume-Rothery F.R.S, B.R. Coles, The transition metals and their alloys, *Advances in Physics*, Taylor and Francis, 1954.
- [326] M.E. Fine, L.D. Brown, H.L. Marcus, Elastic constants versus melting temperature in metals, *Scr. Metall.* 18 (1984) 951–956.
- [327] D.J. Skinner, M. Zedalis, Elastic modulus versus melting temperature in aluminum based intermetallics, *Scr. Metall.* 22 (1988) 1783–1785.
- [328] Melvin M. Vopson, Nassina Rogers, Ian Hepburn, The generalized Lindemann melting coefficient, *Solid State Commun.* 318 (2020) 113977.
- [329] Murahashi N, Kohmoto H, Kohno T, New gas atomizing technique for Nb₃Al intermetallic alloy., *RS Online Proc. Libr. OPL* 364 (1994) 1365.
- [330] C.T. Sims, The Case for Chromium, *JOM* 15 (1963) 127–132.
- [331] Chen D, Chen Z, Wu Y, Wang M, Ma N, Wang H, First-principles study of mechanical and electronic properties of TiB compound under pressure, *Intermetallics* 52 (2014) 64–71.
- [332] Xie D, Guo H, Yang X, Ma, First-principles study of structural, mechanical, and electronic properties of typical iron-containing phases in Al-Cu alloys under different pressures., *Phys. B Condens. Matter* 555 (2019) 112–117.
- [333] Qi L, Jin Y, Zhao X, Yang X, Zhao H, Han P, The structural, elastic, electronic properties and Debye temperature of Ni₃Mo under pressure from first-principles., *J. Alloys Compd.* 621 (2015) 383–388.
- [334] First-principles calculations on structure, elastic and thermodynamic properties of Al₂X (X= Sc, Y) under pressure., *J. Mater. Sci. Technol.* 28 (2012) 155–163.
- [335] Wang Z, Zhang J, Li P, Zhang Y, Jin H, Xu C, Effects of Pressure on the Structural, Mechanical, and Electronic Properties and Debye Temperature of Pd-Based Alloy: First-Principles Calculation., *Phys. Status Solidi B* 258 (2021) 2000490.
- [336] Badding, J. V, High-pressure synthesis, characterization, and tuning of solid state materials, *Annu Rev Mater Sci* 28 (1998) 631–658.
- [337] Grochala, W, Hoffmann, R, Feng, J, Ashcroft, N. W, The chemical imagination at work in very tight places., *Angew Chem Int Ed* 46 (2007) 3620–3642.
- [338] Hemley, R. J., Effects of high pressure on molecules., *Annu Rev Phys Chem* 51 (2000) 763–800.
- [339] Hemley, R. J, Percy W, Bridgman’s second century, *High Press Res* 30 (2010) 581–619.
- [340] Holzapfel, W. B, Physics of solids under strong compression, *Rep Prog Phys* 59 (1996) 28–90.
- [341] Zhang L, Wang Y, Lv Y, Ma Y, Materials discovery at high pressures., *Nat. Rev. Mater.* 2 (2017) 17005.
- [342] McMillan, P, F. Chemistry at high pressure, *Chem Soc Rev* 35 (2006) 855–857.
- [343] McMillan, P, Condensed matter chemistry under ‘extreme’ high pressure-high temperature conditions, *High Press Res* 24 (2004) 67–86.
- [344] McMillan, P. F., Pressing on: the legacy of Percy W. Bridgman., *Nat Mater* 4 (2005) 715–718.
- [345] McMillan, P, New materials from high pressure experiments: challenges and opportunities, *Press Res* 23 (2003) 7–22.

- [346] McMillan, P. F., New materials from high-pressure experiments, *Nat Mater* 1 (2002) 19–25.
- [347] Chen Z, Zhang P, Chen D, Wu Y, Wang, M, Ma N, Wang H, First-principles investigation of thermodynamic, elastic and electronic properties of Al₃V and Al₃Nb intermetallics under pressures, *J. Appl. Phys.* 117 (2015).
- [348] Durukan İ K, Mechanical, vibration, and optical properties of IrAl intermetallic compound via DFT calculations: high-pressure effect., *Phys. Scr.* 98 (2023) 075903.
- [349] Liu Y, Huang H, Pan Y, Zhao Z, Liang, First-principles study on the phase transition, elastic properties and electronic structure of Pt₃Al alloys under high pressure, *J. Alloys Compd.* 597 (2014) 200–204.
- [350] Mouhat F, Coudert, F.X, Necessary and sufficient elastic stability conditions in various crystal systems., *Phys. Rev. B* 90 (2014) 224104.
- [351] G.R. Stewart, Superconductivity in the A15 structure, *Phys. C* 514 (2015) 28–35.
- [352] Jianzuo Ma, Weiguo Li, Guoxin Yang, Shifeng Zheng, Yi He, Xin Zhang, Modeling the pressure-dependent melting temperature of metals, *Phys. Earth Planet. Inter.* 309 (2020) 106602.