CHAPTER 5

ELECTRONIC BANDSTRUCTURE, THERMAL AND SUPERCONDUCTING PROPERTIES OF Ti_3M (M = Au, Pt, AND Ir) COMPOUNDS

5.1 INTRODUCTION

The first studies on the binary inter metallic compounds, the A15 (Cr_3O-type phases) family has been intensively investigated (Beck1963, Nevit et al 1977, Dew-Hughes 1975). Superconductors with the A15 structure and A_3X composition, generally show very interesting superconducting properties, i.e. high critical fields and temperatures. Moreover, there is also great deal of interest in the superconducting A15 materials which have high transition temperature (Mohan Rao et al 1987, Paduani et al 2009) and high critical current values (Francavilla 1978). High-quality, large single crystals of the A15 compounds are necessary in a variety of physical properties studies such as investigations of band structure and lattice disorder. The high temperature superconductors of A15 structure are also known to be strong electron-phonon coupling materials (Paduani et al 2007). A comprehensive review of lattice and electronic properties of these compounds have been written by Wager & Goldberg (1973) and a review of the critical superconducting parameter has been done by Dew-Hughes (1975). Lattice parameters of Ti_3Pt increased with increasing Pt content over the range 23-27 at % Pt. Ti_3Pt becomes superconducting at 0.58K (Matthias et al 1963). Tc of

Ti_3Ir and Ti_3Au are 4.3K and 0.49K respectively (Bongi1976). The richness of phenomena and anomalous physical properties observed in these materials has motivated the study of the properties of their fundamental electronic structures. Hence, the basic electronic properties of these materials, have carried out the electronic band structure studies using the well-known and versatile TB-LMTO method, and hence the results of electronic, ground state, thermal and superconducting properties of Ti_3M (M = Au, Pt, and Ir) are presented here. The mechanical and thermal properties of the above mentioned compounds are reported earlier (Rajagopalan et al 2012), but no one calculate superconducting properties. The results have been analyzed and compared with the literature data.

5.2 CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

Titanium forms a number of inter metallic compounds with A15 structure. Among them, the compounds Ti_3M (M = Au, Pt, and Ir) are interesting due to their thermal and superconducting properties. Space group of Ti_3M (M = Au, Pt, and Ir) are same as Pm-3n (no.223). The atomic position in Ti_3M (M = Au, Pt, and Ir) are, Ti: 0, 1/2, 1/4 and Au or Pt or Ir: 0, 0, 0. The electronic configurations of elements in these materials are Ti: [Ar] $3d^2 4s^2$; Au: [Xe] $4f^{14}5d^{10}6s^1$; Pt: [Xe] $4f^{14}5d^9 6s^1$and Ir: [Xe] $4f^{14}5d^7 6s^2$. Self-consistent band structure calculations of A-15 compounds (Ti_3M) have been performed using the TB-LMTO method, with the atomic sphere approximation (ASA) (Andersen et al 1984, Skriver1984, Andersen 1975, Andersen et al 1986).

The Von Barth-Hedin local density form for the exchange and correlation potential (Von Barth et al 1972) have been used. These calculations are based on the density functional theory of Hohenberg & Sham, Kohn & Sham (1964), (1965) with the local density approximation. The total and partial DOS have been determined by means of the tetrahedron method. All the muffin-tin radii and number of k-points were varied to ensure total energy convergence. The k-mesh in the irreducible wedge of the Brillouin zone contained in Ti_3M (M = Au, Pt, and Ir) have same as 10 irreducible k mesh points from 64 (4 4 4). The basis set included s, p, d and f orbitals for all systems. The ground-state properties were calculated for the lattice parameters that correspond to the minimum of the total energy. The structure is shown in Figures 5.1 – 5.3.

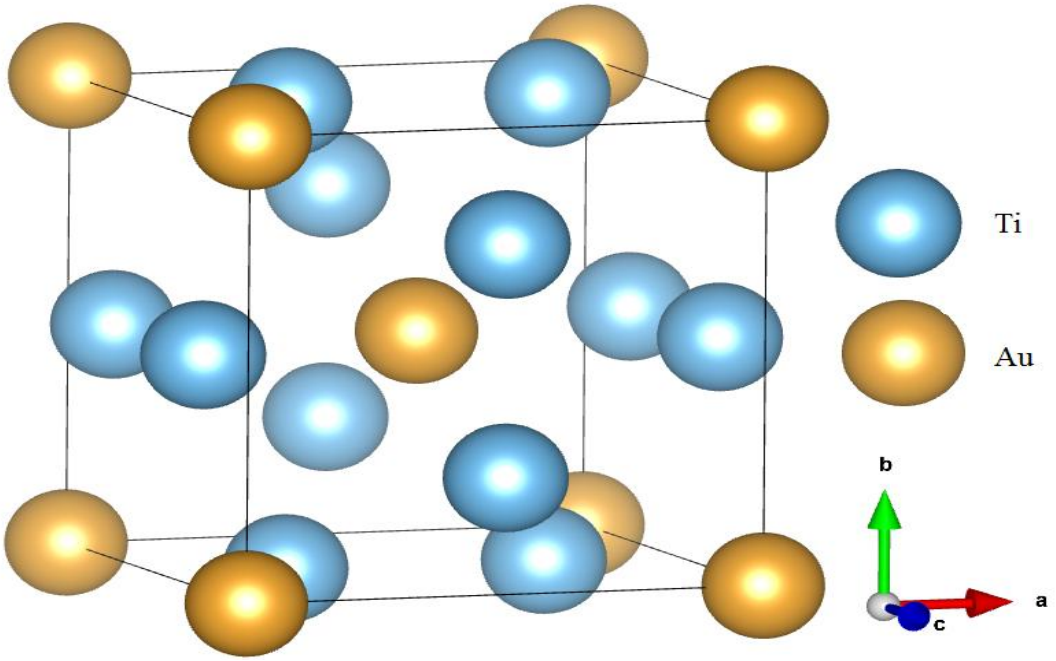

Figure 5.1 Cubic structure for Ti_3Au

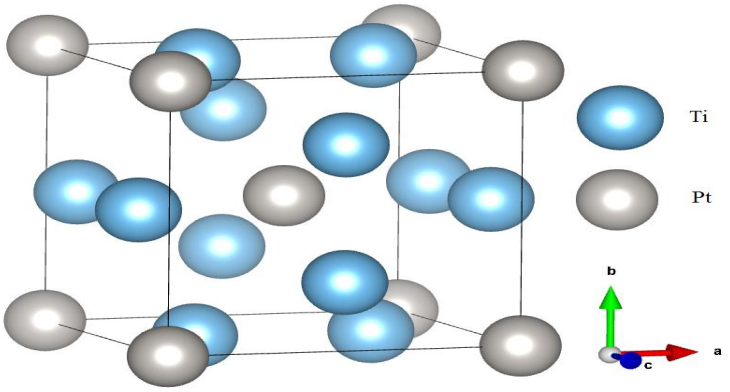

Figure 5.2 Cubic structure for Ti_3Pt

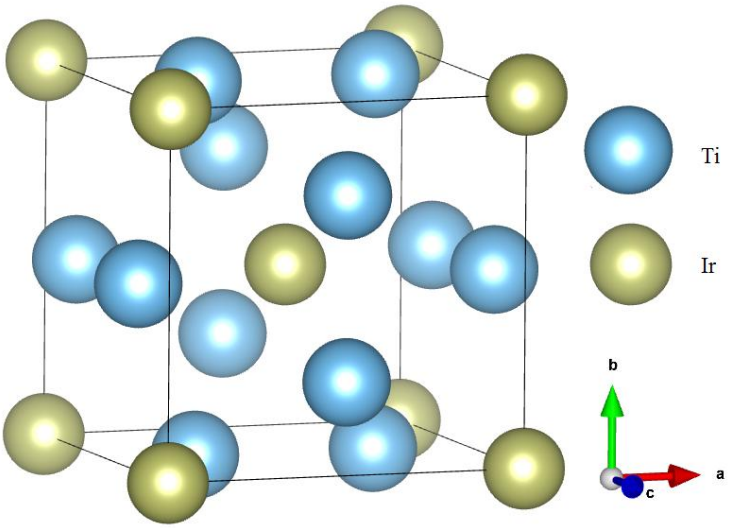

Figure 5.3 Cubic structure for Ti_3Ir

5.3 TOTAL ENERGY CALCULATION AND RELATED PROPERTIES

All the electronic properties such as the DOS and energy bands were calculated for the equilibrium lattice parameters. For each case, the equilibrium lattice parameters were obtained by minimizing the electronic total energy (E_T) with respect to the cell volume. The plots of total energy as a function of volume for Ti_3M (M = Au, Pt, and Ir) are shown in Figure 5.4.

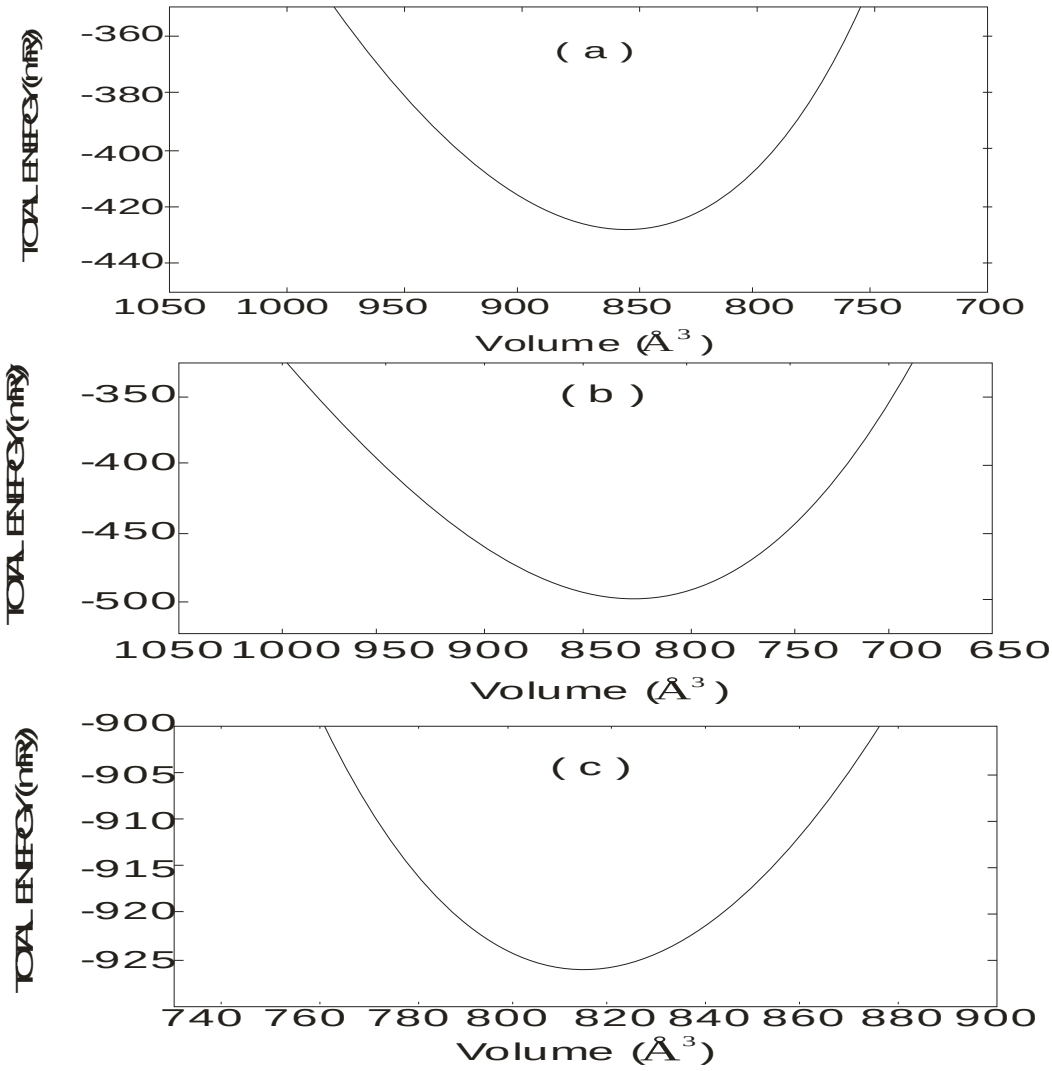

Figure 5.4 Variation of total energy (with reference to - 86239.000, - 83847.000, - 81504.000) Ry with cell volume for (a) Ti_3Au, (b) Ti_3Pt, and (c) Ti_3Ir

The curve was obtained by fitting the E_T - V data to Murnaghan's equation of state (Murnaghan 1944) (3.30)

$$E(V) = V\frac{B_0}{B_0^{'}}\left[\frac{\left(V_0/V\right)^{B_0^{'}}}{B_0^{'}-1}+1\right] + \text{const.} \qquad (5.1)$$

Where B_0 is the bulk modulus and B'_0 is the pressure derivative of B_0. The equilibrium lattice parameters were obtained, by minimizing the total energy by varying the cell volumes of Ti_3M (M = Au, Pt, and Ir) alloys. The variations of lattice constants are in compliance with the variation of the size of atoms in their compounds. A comparison of experimental (Somi reddy 1983) lattice parameters of Ti_3M (M = Au, Pt, and Ir) are given in Table 5.1.

Table 5.1 Comparison of the calculated lattice parameters with the experimental results

Alloys	Lattice parameter (Å)	
	Present	Experimental
Ti_3Au	5.0875	5.0960[a]
Ti_3Pt	4.9752	5.0330
Ti_3Ir	5.0048	5.0065[a]

(a) Somi Reddy et al (1983)

5.4 ELECTRONIC BAND STRUCTURE CALCULATIONS

Transition metals have large *d*-electron shells, and are characterized by high binding energy (Kittel 2008). The electronic band structures of Ti_3M (M = Au, Pt, and Ir), along the high symmetry directions of the Brillouin zone, are displayed in Figures 5.5- 5.7.

The Fermi level is set to 0 Ry. They are also very strongly hybridized. Highly dense accumulation of p- and d- bands occurs around the Fermi energy for all the three compounds. A relatively larger value of E_F for Ti_3Au is attributed to the more occupied p- and d- bands, relative to other two compounds. The band structures show the Fermi energy decrease with decrease in their atomic number of M element. The Fermi energies of Ti_3M (M = Au, Pt, and Ir) are: 0.70717 Ry, 0.73892 Ry, and, 0.737557 Ry, respectively.

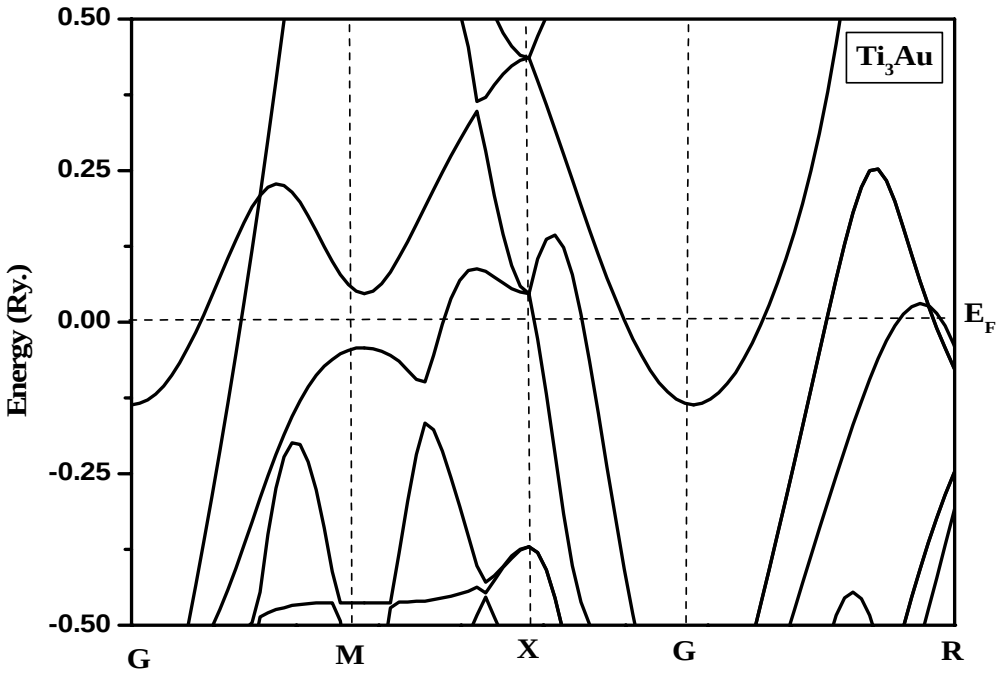

Figure 5.5 Energy band structure for Ti_3Au

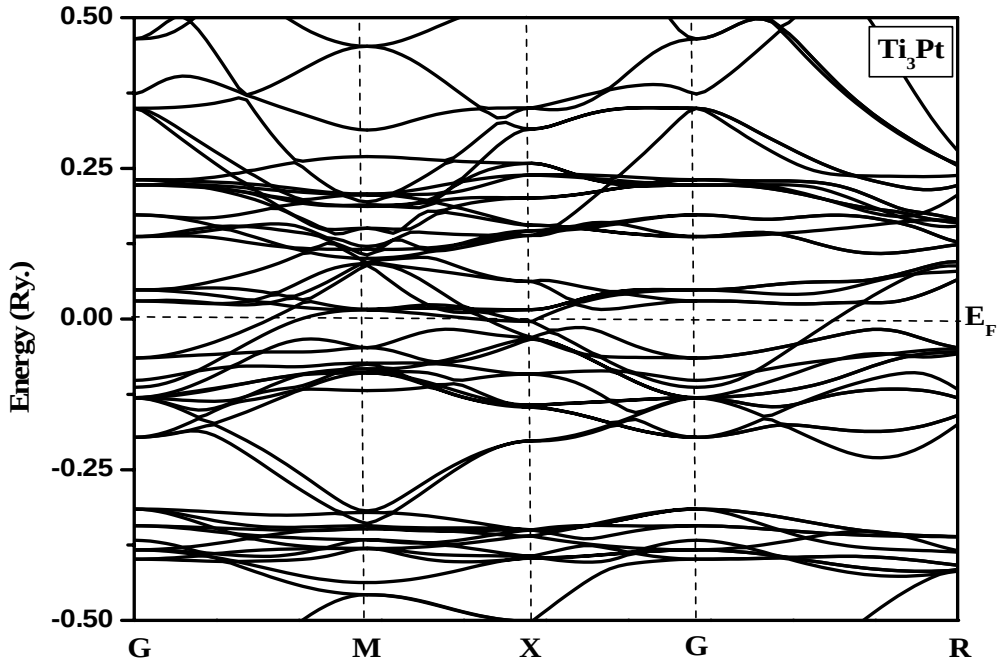

Figure 5.6 Energy band structure for Ti_3Pt

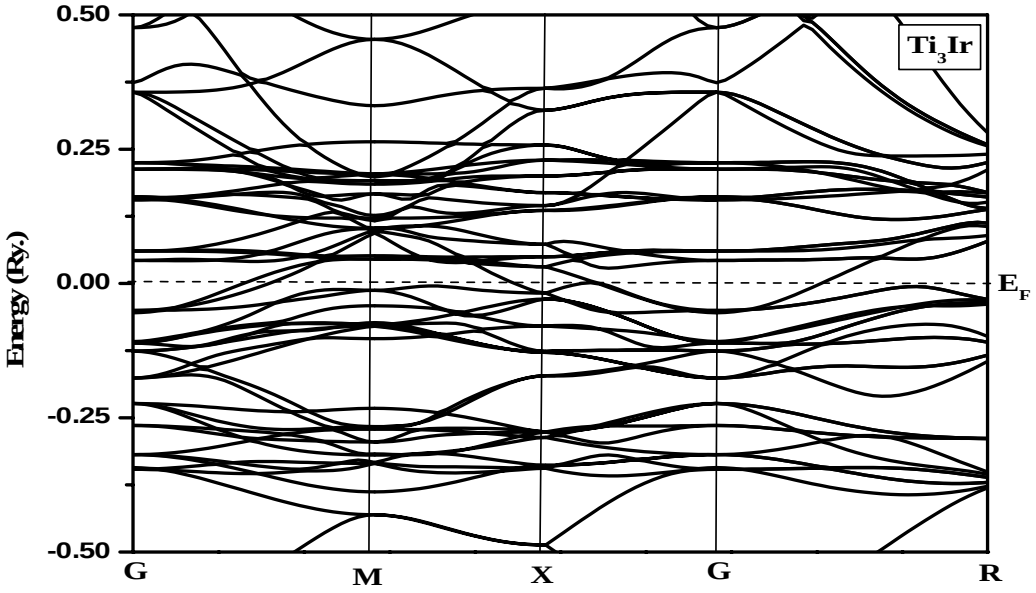

Figure 5.7 Energy band structure for Ti_3Ir

5.5 ELECTRONIC DENSITY OF STATES

The total and partial DOS of all the three alloys namely Ti_3M (M = Au, Pt, and Ir), are presented in Figures 5.8-5.19, respectively. The DOS at E_F for Ti_3M (M = Au, Pt, and Ir), are presented in Table 5.2. It can be seen from Figures 5.8-5.19 that d states dominated the DOS of the intermetallic compound over all contribution from s, p, and f states. The high DOS around E_F is, evidently, due to the strong pile up of p- and d- bands in all the three compounds. The DOS at the Fermi level is almost exclusively of d- character. The DOS at Fermi level decreases with the decrease of the atomic number of M element.

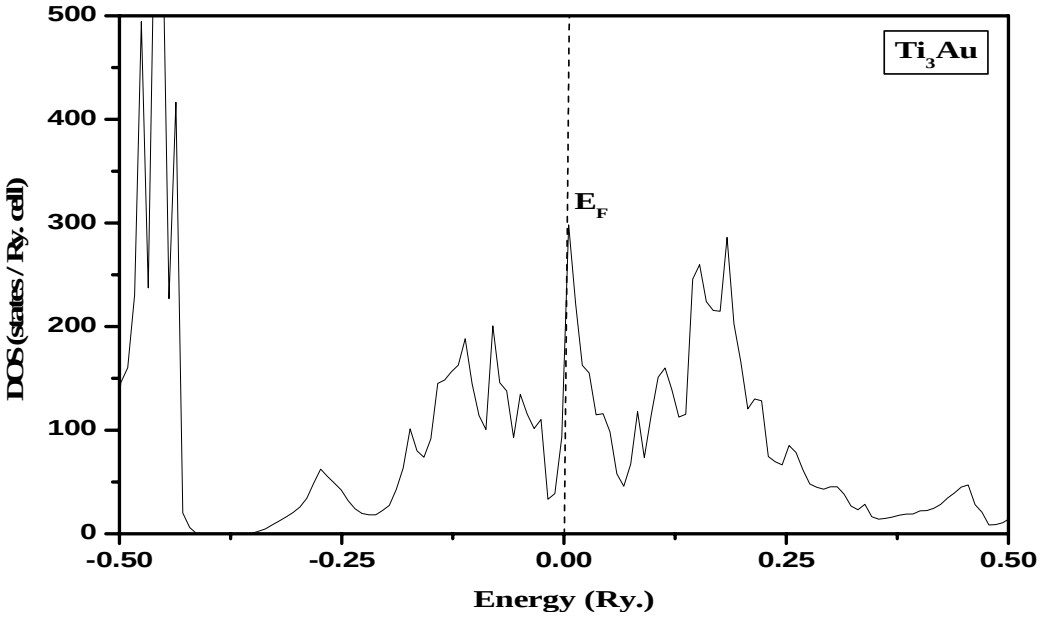

Figure 5.8 Total density of states for Ti_3Au

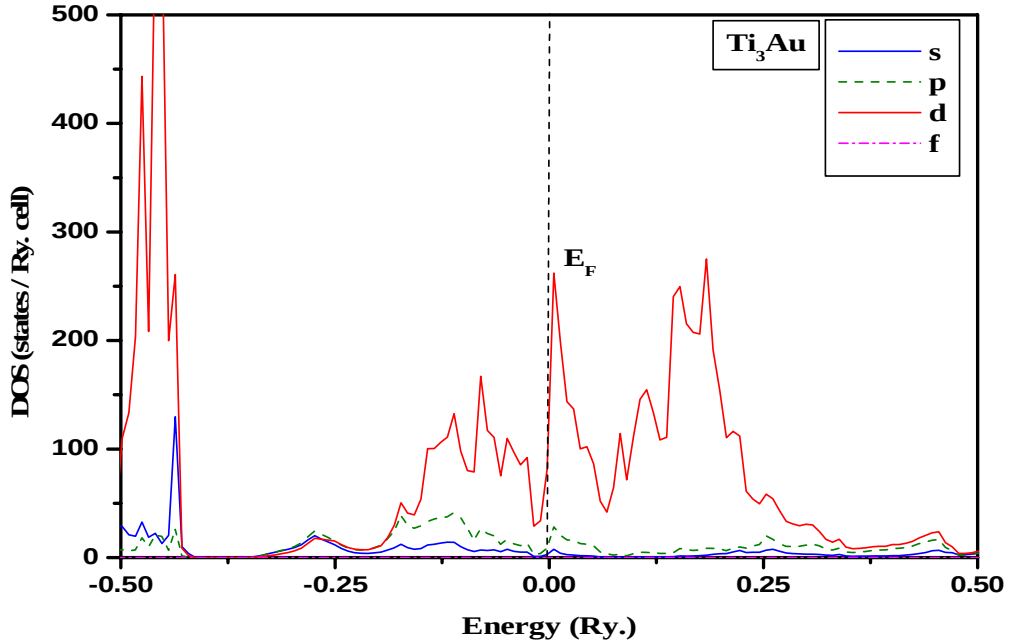

Figure 5.9 Partial density of states for Ti_3Au

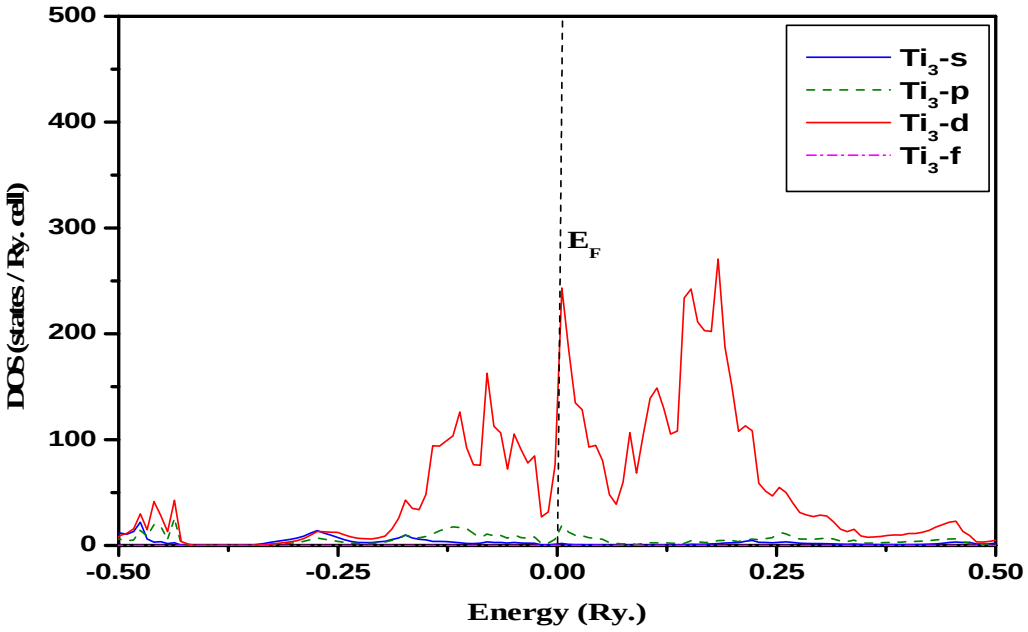

Figure 5.10 Partial density of states for Ti_3 of Ti_3Au

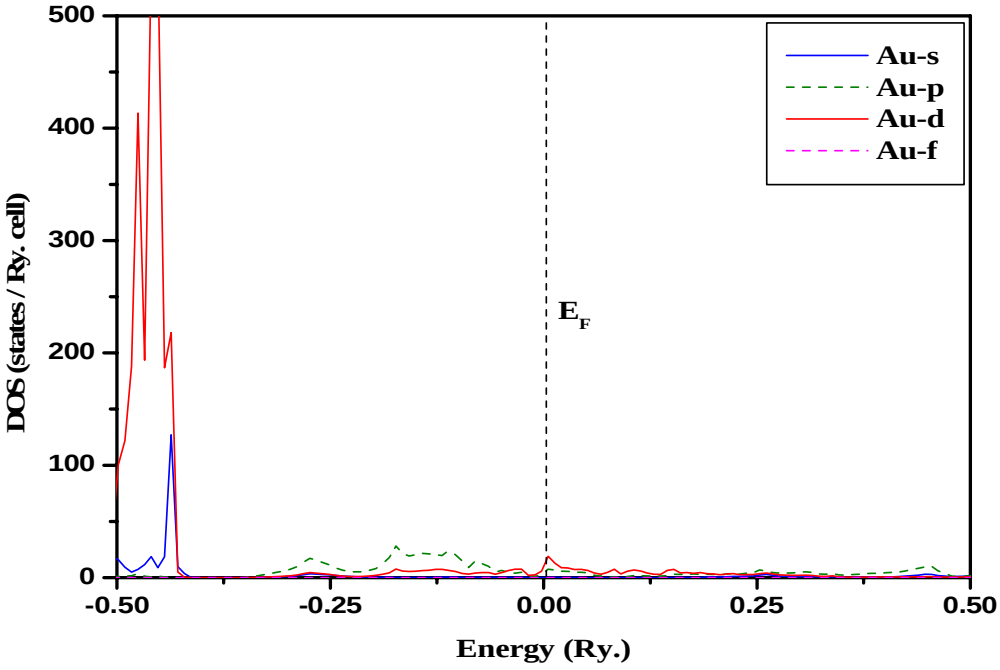

Figure 5.11 Partial density of states for Au of Ti_3Au

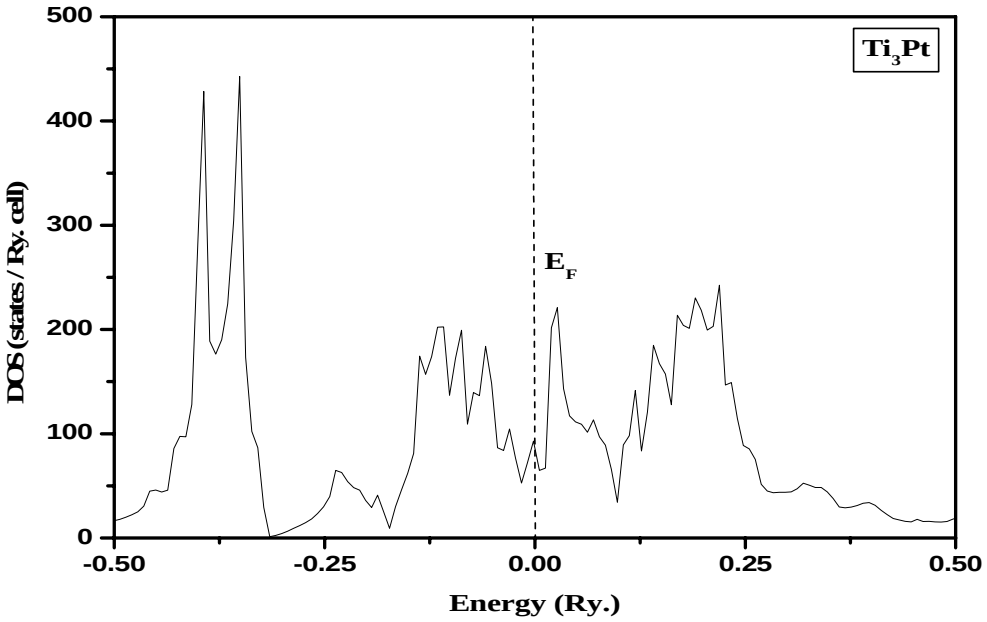

Figure 5.12 Total density of states for Ti_3Pt

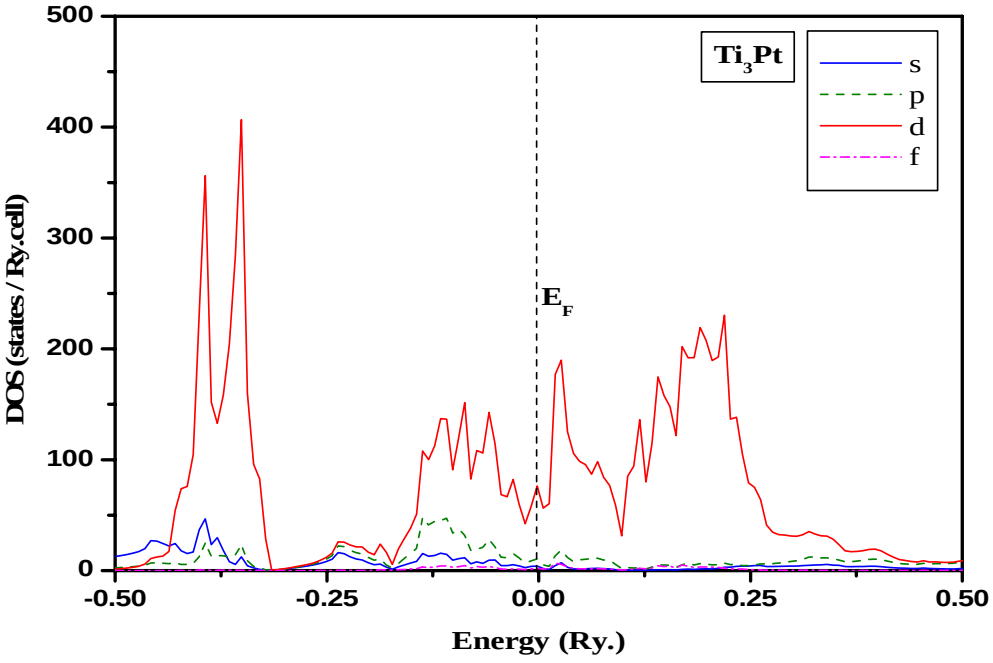

Figure 5.13 Partial density of states for Ti_3Pt

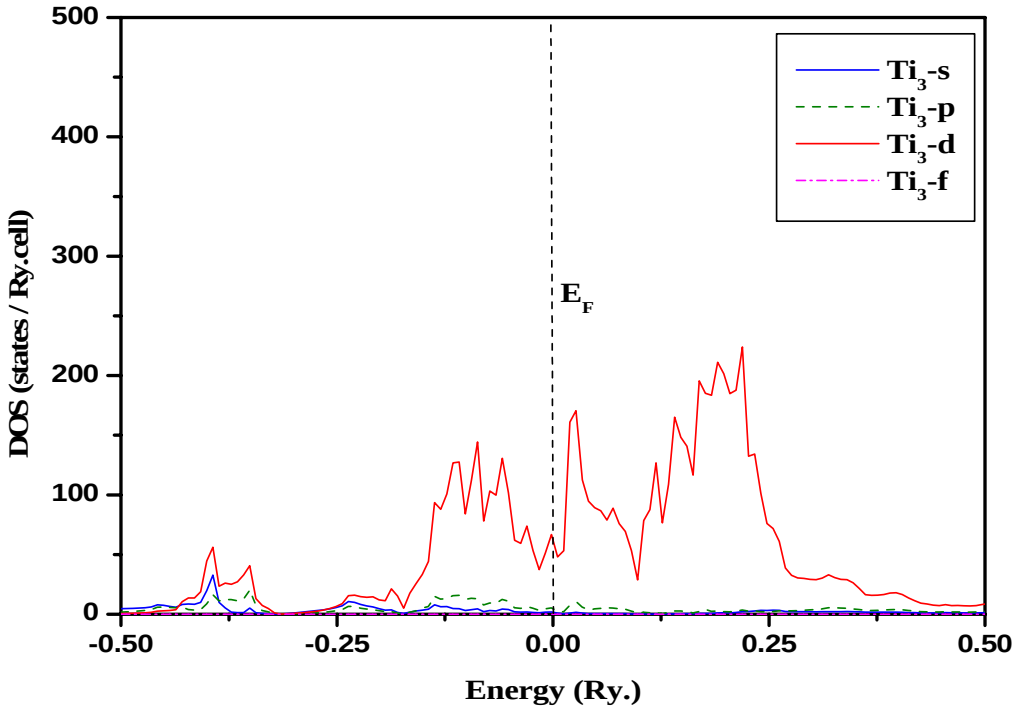

Figure 5.14 Partial density of states for Ti_3 of Ti_3Pt

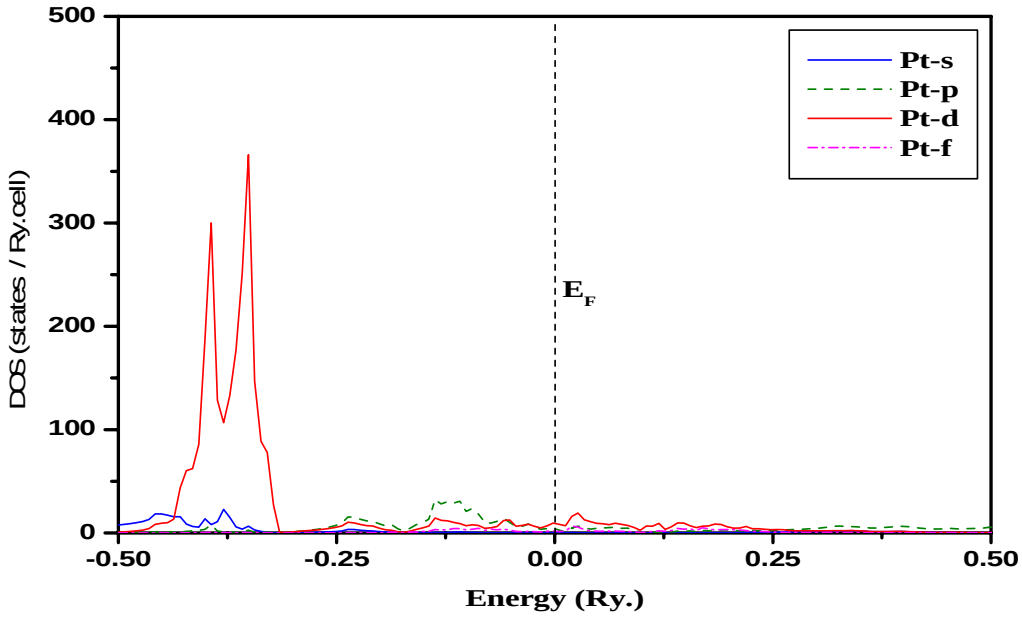

Figure 5.15 Partial density of states for Pt of Ti_3Pt

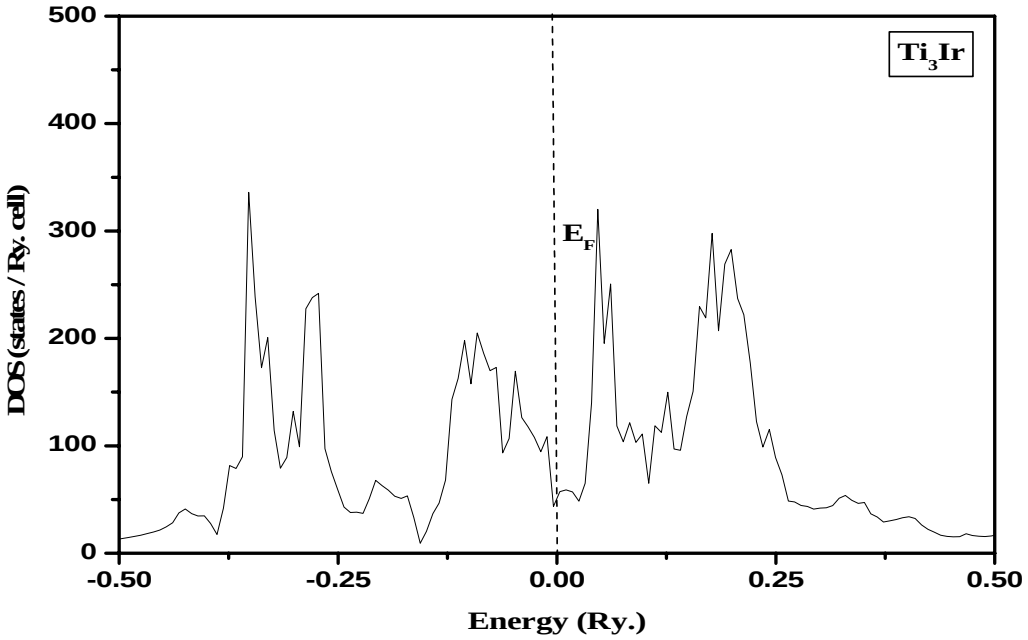

Figure 5.16 Total density of states for Ti_3Ir

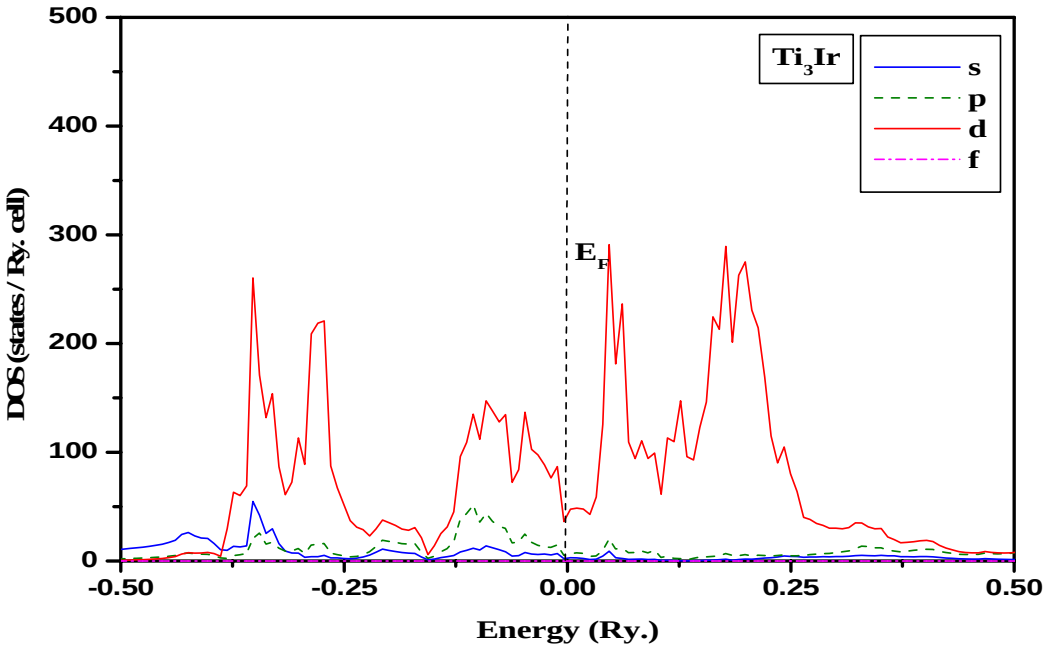

Figure 5.17 Partial density of states for Ti_3Ir

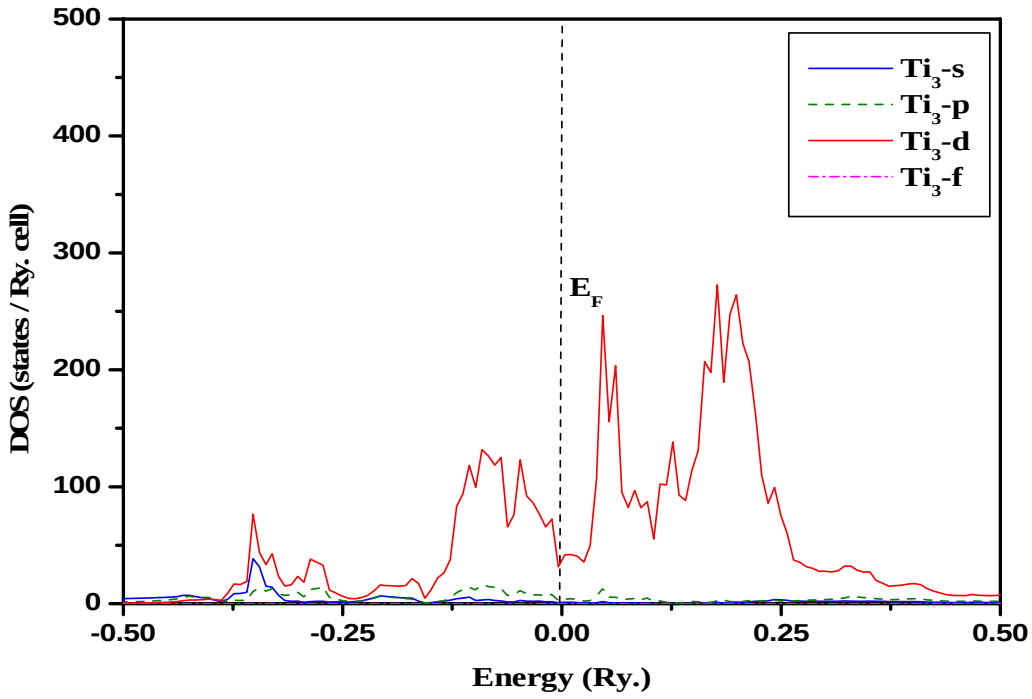

Figure 5.18 Partial density of states for $Ti_3$of Ti_3Ir

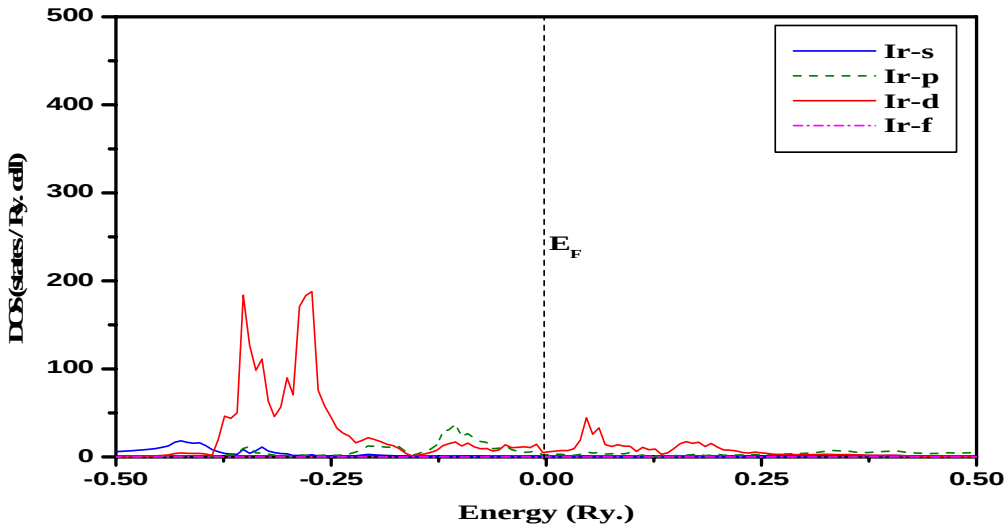

Figure 5.19 Partial density of states for Ir of Ti_3Ir

Table 5.2 Electronic density of states at the Fermi energy for Ti_3M (M = Au, Pt, and Ir) for *s*-, *p*-, and *d*- bands of various atomic elements

Bands	DOS at E_F ((states/Ry)/atom)											
	Ti_3Au				Ti_3Pt				Ti_3Ir			
	Ti	Au	E	Total	Ti	Pt	E	Total	Ti	Ir	E	Total
s	1.915	0.262	5.416	7.593	0.947	0.080	0.880	1.907	1.237	0.189	1.562	2.988
p	18.962	7.702	1.726	28.39	2.556	2.404	0.251	5.211	3.860	2.567	0.209	6.636
d	243.292	18.918	0	262.21	48.116	8.319	0	56.435	41.774	5.935	0	47.709

5.6 THERMAL PROPERTIES

The cohesive energy and heat of Formation of Ti_3M (M = Au, Pt, and Ir) compounds are calculated from the given formulae (Vipul Srivastava et al 2012) and values are given in Table 5.3.

$$E_{coh}^{AB} = \left[E_{atom}^{A} + E_{atom}^{B} - E_{total}^{AB} \right] \tag{5.2}$$

$$E_{form}^{AB} = \left[E_{total}^{AB} - \left(E_{solid}^{A} + E_{solid}^{B} \right) \right] \tag{5.3}$$

The Debye temperature (Θ_D) and Grüneisen constant (γ_G) are important parameters, related to the thermal properties of materials. To calculate the thermal properties of a vibrating Debye lattice, we have used the Debye-Grüneisen model (Debye 1912).In the present work, the Debye temperature is calculated using the Equation (3.50). The Grüneisen constant (γ_G) is related to the Debye temperature (Θ_D) and the volume of the unit cell (V) by the relation (3.52) (Shashikala et al 1987). The calculated values of Θ_D and γ_G are shown in Table 5.3. The Debye temperature is found to agree reasonably well with the existing experimental reports.

The electronic specific heat coefficient (γ) is related to the density of states N (E_F) and the electron phonon mass enhancement factor (λ) by the expression (3.53). Hence, this quantity can be obtained from the calculated values of N (E_F) and λ. The values of the electronic specific heat coefficient (γ) for Ti_3M (M= Au, Pt, and Ir) are given in Table 5.4.

5.7 SUPERCONDUCTING PROPERTIES

The superconducting transition temperature is calculated using McMillan's formula (McMillan 1968) in (3.58). From Table 5.4 that among the three compounds Ti_3Ir has the highest T_C value. The T_C values estimated by the present work for Ti_3M (M = Au, Pt, and Ir) are agreeing with the experimental values reported earlier (Blaugher et al 1969, Muller 1980). The λ value of Ti_3Pt is agreed with the experimental values (Turchi et al 1983). No such earlier results are available for γ of Ti_3M (M = Au, Pt, and Ir) in the literature for comparison. The atomic number of M increases in the values of the superconducting properties like λ and T_C decrease for Ti_3M (M = Au, Pt, and Ir). The electron-phonon coupling constant (λ) can be estimated, using the electronic band structure results from the relation (3.51).

Table 5.3 Equilibrium Wigner-Seitz radii (r_0), bulk modulii (B_0), cohesive energy (Ec), heat of formation (-ΔH), Debye temperature (Θ_D) and Grüneisen constant (γ_G) for Ti_3M (M = Au, Pt, and Ir)

Alloys	r_0 (a.u.)	B_0 (GPa)	Ec (Ry.)	-ΔH(mRy)	Θ_D(K)		γ_G
					Present	Exp.	Present
Ti_3Au	2.47446	437.00	2.1	0.10	380.2	385[a][14]	0.72
Ti_3Pt	2.41987	178.71	2.4	0.17	241.0	-	1.09
Ti_3Ir	2.43426	178.39	2.6	0.16	242.7	238[b][30]	1.90

(a) Bongi(1976) (b) Junod (1983)

Table 5.4 Electron-phonon interaction constant (λ), electronic specific heat coefficient (γ), and superconducting transition temperature (T_C) for Ti_3M (M = Au, Pt, and Ir)

Alloys	λ		γ	Tc(K)	
	Present	Exp.	($mJmol^{-1}K^{-2}$)	Present	Exp.
Ti_3Au	0.28	-	14.73	0.09	<0.015[a] 0.5[c]
Ti_3Pt	0.50	0.73[d]	18.69	2.00	0.49[a] 0.486[b]
Ti_3Ir	0.62	-	24.04	5.00	4.3[a] 5.4[b]

(a) Bongi (1976), (b) Blaugher et al (1969), (c) Muller (1980), (d) Turchi et al (1983).

5.8 SUMMARY

The electronic band structure studies of titanium based A15 superconductors Ti_3M (M = Au, Pt, and Ir) are carried out, for the first time by using the TB-LMTO method. The ground state properties such as equilibrium lattice parameters and primitive cell volume have been obtained by fitting the electronic total energy with the Murnaghan equation of state and are in good agreement with the experimental results. The electronic band structures show a strong hybridization between p- and d- bands and are also narrowly piled up around the Fermi energy for all these three materials and it is also evident in the density of states results. Furthermore, it is found that the bandstructure and related properties at the Fermi energy are dominated by the d- bands originating mainly from titanium in all the three alloys. The density of states at the Fermi energy is found to be strongly influenced by the d- bands of atoms of Ti_3M (M = Au, Pt, and Ir) respectively contribute predominantly at the Fermi level for all the materials. As a consequence, the

electron-phonon interaction parameter, and electronic specific heat have been found to decrease with the increase the atomic number of M in all three superconducting compounds. The calculated results are observed to be in good agreement with the available experimental results existing in the literature. Thus the present studies have provided a better understanding of the fundamental electronic, thermal and superconducting properties of these three materials.