

Site preference of Zr in Ti_3Al and phase stability of Ti_2ZrAl

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Abstract. The site preference of Zr atoms in Ti_3Al and the phase stability of Ti_2ZrAl are examined using first-principles electronic structure total energy calculations. Of the sixteen possible ways in which Ti, Zr and Al atoms can be arranged, in the lattice sites corresponding to $D0_{19}$ structure of Ti_3Al , to obtain Ti_2ZrAl , it is shown that Zr atoms prefer to get substituted at the Ti sites. It is further shown that among the seven crystal structures considered, $D0_{19}$ -like and $L1_2$ -like are the competing ground-state structures of Ti_2ZrAl . The above results are in agreement with the experimental results reported in the literature. Calculated values of equilibrium lattice parameters, heat of formation and bulk modulus of Ti_2ZrAl are presented. The basis for the structural stability and bonding are analysed in terms of the density of states. Between the two possible $B2$ -like structures, Ti_2ZrAl shows enhanced stability for the one where Zr is substituted in the Ti sublattice, which again is in agreement with the experimental observation.

Keywords. Site preference; phase stability; first-principles calculations; Ti_3Al .

1. Introduction

Ti_3Al has been studied extensively during the past two decades because of its low density, good high-temperature strength and oxidation resistance at elevated temperatures (Lipsit 1993). However, Ti_3Al suffers from poor room-temperature ductility and fracture toughness. There have been a number of studies to understand the effects of alloying additions on the properties of Ti_3Al based alloys. Substitutional alloying affects the physical properties at the microscopic level and hence knowledge of substitutional behaviour of alloying additions is not only of great practical interest but also of fundamental theoretical interest. Several first-principles studies (Xu and Freeman 1994; Song *et al* 1998) show that the site preference of alloying elements is a key factor in describing properties such as twin-boundary energy and dislocation mobility of the alloys. Several techniques such as X-ray diffraction, transmission electron microscopy, atom probe field ion microscopy (Munroe and Baker 1991; Larson and Miller 1998), etc are available for experimental investigation of site occupancy. Over the years, various models have also been developed to study the substitutional behaviour of alloying additions theoretically. The first among them is the Ising model with nearest neighbour effective pair interactions and it was studied in detail using the cluster variation method (Wu *et al* 1989). Ruban and Skriver (1997) have developed a model based on the empirical parametrization of the ordering energy (obtained from first-principles cal-

ulation of the total energy of partially ordered alloys), which is the analogue of the rectangular d -band model of the cohesive energy developed by Friedel (1969). A thermodynamic model incorporating results of first-principles total energy calculations introduced by Woodward and Kajihara (1998) describes substitutional behaviour of alloying additions in terms of the change in the chemical potentials of the system obtained by minimization of free energy. Jiang (1999) modeled sublattice occupancy in ternary intermetallic compounds by an analytical approach wherein an atom pair transition occurs between two sublattices whenever the energy change caused by this process is negative. Another approach, which is used in the present work, is to compare the heat of formation of pure and defect unit cells from the first-principles calculation of the total energy of the system (Kim *et al* 2000).

In this paper, we present the results of a systematic study of site preference of Zr atoms in Ti_2ZrAl by considering all 16 ways of arranging (henceforth referred to as decoration) Ti, Zr and Al atoms at the atomic sites in the $D0_{19}$ unit cell of Ti_3Al consistent with the required stoichiometry. The stability of the crystal structure of Ti_2ZrAl is then examined by considering six other competing structures. Section 2 describes the possible inequivalent decorations of $D0_{19}$ unit cell to study the site preference of Zr atoms in Ti_3Al . The various crystal structures employed to understand the phase stability of Ti_2ZrAl are also described. Section 3 gives the computational details and in §4, we discuss the results of the calculations. Section 5 analyses the density of states of Ti_2ZrAl to obtain information regarding the structural stability and bonding. The last section is devoted to a brief summary of the results.

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2. Crystal structure details

Several engineering alloys, $Ti_{3-x}M_xAl$ (M is a transition metal), based on $a_2-D0_{19}-Ti_3Al$, have been developed in the recent times. It is believed that in this structure, the M atoms occupy the Ti sites. Banerjee (1995) and Yang *et al* (2000) have confirmed that Zr indeed gets substituted at the Ti sites in Ti_3Al . The X-ray powder diffraction study (Sornadurai *et al* 2000a) reports that Ti_2ZrAl remains in the $D0_{19}$ structure of the parent compound, Ti_3Al .

In the $D0_{19}$ unit cell there are two formula units of atoms arranged in two planes. Let $\{A, B, C, D\}$ and $\{E, F, G, H\}$ refer to the atomic positions in the planes I and II. The coordinates of these atoms are the following:

- I: (1) A (Ti)(1/6, 5/6, 3/4); (2) B (Ti)(1/6, 1/3, 3/4); (3) C (Al)(2/3, 1/3, 3/4); (4) D (Ti)(2/3, 5/6, 3/4);
 II: (5) E (Al)(1/3, 2/3, 1/4); (6) F (Ti)(1/3, 1/6, 1/4); (7) G (Ti)(5/6, 1/6, 1/4); (8) H (Ti)(5/6, 2/3, 1/4).

By using the freedom in the choice of directions of the basis vectors \vec{a} and \vec{b} and the origin, it can be shown that all the 24 ways of arranging atoms in each of the planes (considered in isolation) of the $D0_{19}$ unit cell are equivalent. However, when both the planes are considered together, there are many inequivalent ways of arranging the atoms. After accounting for the symmetries present in the system, it can be shown that there are 16 inequivalent decorations of the atomic sites $A B C D E F G H$ (with 4 Ti , 2 Al and 2 Zr) as given in table 1. Since each of these decorations of $D0_{19}$ unit cell imply different interplanar and intraplanar atomic interactions, it is necessary to calculate the total energy of each of these to

determine the structure with lowest energy. Since the equilibrium lattice parameters of each of these decorations can be different, in principle, it is important to optimize the total energy by relaxing the lattice parameters (a and c) simultaneously. Hence, we have carried out total energy calculations, for each of the 16 decorations, at 11×11 different values of each of (a , c) in the range $0.92 \leq a/a_{\text{expt}}$, $c/c_{\text{expt}} \leq 1.10$, where a_{expt} and c_{expt} are the values of the lattice parameters obtained in the experiments. It may be noted that the symmetry of the unit cell is retained to be the same as that of the parent compound, but the symmetry of the basis lowered, in these calculations. To find the site preference of Zr atoms in Ti_3Al , the heats of formation were calculated for each of the above 16 decorations using their respective equilibrium total energies.

To examine the phase stability of Ti_2ZrAl in relation to the $D0_{19}$ -like structure, six other competing structures (described below) are also studied. Banerjee (1995) has reported that Zr atoms get substituted at the Ti sublattice in the $B2(cP2)$ ternary phase with Ti_2AlZr composition. The $B2(CsCl)$ structure can be described in terms of the two interpenetrating sc lattices with one lattice displaced with respect to the other by the vector $\frac{1}{2}\langle 111 \rangle$. An equivalent way of describing the $B2$ structure is to consider a sc lattice with a diatomic basis. For the $B2-Ti_2ZrAl$ we have constructed two $B2$ -like unit cells with a 4 atom basis obtained by stacking two $B2(CsCl)$ unit cells one over the other to ensure the desired composition. In one of the $B2$ -like cells (designated as $B2-I$) the stacking is $TiAlTiZr$, while in the other ($B2-II$) it is $TiTiAlZr$. These are the only two inequivalent stacking for Ti_2ZrAl (with 4 atoms) in the $B2$ -like unit cell. Sketches of the unit cells of the crystal structures considered for Ti_2ZrAl are given in figure 1.

Table 1. Lattice constants (in a.u.) and heat of formation, ΔH (in eV/atom) for the 16 inequivalent decorations of the $D0_{19}$ unit cell obtained by substituting one of the Ti atoms with Zr in Ti_3Al . $A B C D E F G H$ are labels corresponding to the 8 atomic positions in the $D0_{19}$ unit cell.

A	B	C	D	E	F	G	H	a_0	c_0	ΔH
Ti	Ti	Ti	Ti	Al	Al	Zr	Zr	11.0795	8.9231	-0.1329
Ti	Ti	Ti	Al	Ti	Al	Zr	Zr	11.0592	8.8717	-0.2374
Ti	Ti	Ti	Al	Ti	Zr	Zr	Al	11.1035	8.8717	-0.0802
Ti	Ti	Ti	Al	Al	Zr	Zr	Ti	11.1035	8.8717	-0.0801
Ti	Ti	Ti	Zr	Ti	Al	Al	Zr	10.8836	9.2137	-0.1409
Ti	Ti	Ti	Zr	Ti	Al	Zr	Al	10.8836	9.2137	-0.1480
Ti	Ti	Ti	Zr	Al	Zr	Al	Ti	11.0374	8.9613	-0.1899
Ti	Ti	Al	Al	Ti	Ti	Zr	Zr	11.1013	8.8502	-0.1706
Ti	Ti	Al	Al	Ti	Zr	Zr	Ti	11.1035	8.8717	-0.1378
Ti	Ti	Al	Al	Zr	Zr	Ti	Ti	11.1241	8.8523	-0.1064
Ti	Ti	Al	Zr	Ti	Ti	Al	Zr	10.8833	9.2131	-0.1363
Ti	Ti	Al	Zr	Ti	Al	Zr	Ti	10.8833	9.2131	-0.0991
Ti	Ti	Al	Zr	Ti	Ti	Zr	Al	10.8833	9.2131	-0.1373
Ti	Ti	Al	Zr	Ti	Zr	Al	Ti	11.0374	8.9434	-0.1418
Ti	Ti	Al	Zr	Ti	Al	Ti	Zr	10.8833	9.2131	-0.0990
Ti	Ti	Al	Zr	Al	Zr	Ti	Ti	10.9937	8.9613	-0.2730

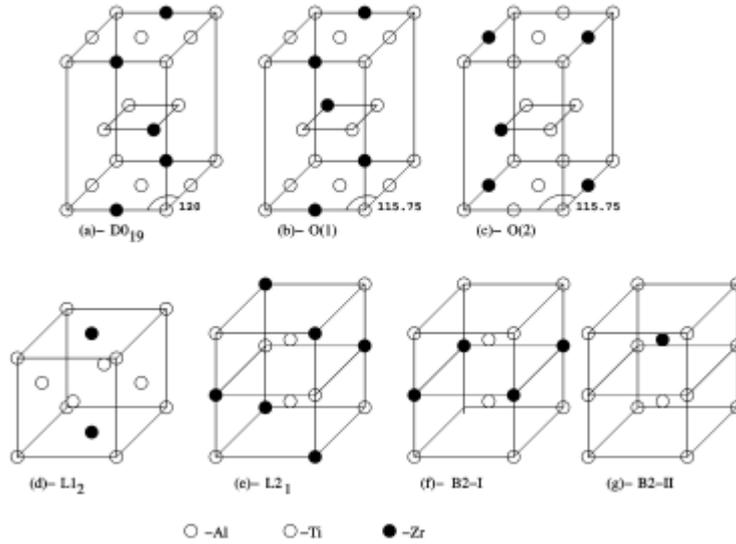


Figure 1. Crystal structures considered for Ti_2ZrAl : (a) is the DO_{19} -like unit cell with Zr atoms substituted in their preferred Ti sites, (b) and (c) are the hexagonal equivalent of the O phase unit cell, (d) is the unit cell of the $L1_2$ -like structure, (e) is the $L2_1$ equivalent unit cell, and (f) and (g) are the B_2 ($cP2$)-based unit cells.

A ternary ordering for the bcc Ti_2NbAl , where all the three atoms occupy distinct sublattices is more likely to lead to a structure based on $L2_1(Fm3m)$ symmetry (Banerjee *et al* 1988) which is also being inferred by Mark Asta *et al* (1995). Hence we consider $L2_1$ structure for Ti_2ZrAl in this calculation. In view of the fact that both DO_{19} and $L1_2$ structures are degenerate (Banerjee and Cahn 1983; Hong *et al* 1991; Watson and Weinert 1998) for Ti_3Al and Zr_3Al , an $L1_2$ -like structure also is considered as a possible structure for Ti_2ZrAl . Since ordered ternary orthorhombic phase of Ti_2NbAl and Ti_2VAl with $Cmcm$ space-group symmetry are observed (Banerjee *et al* 1988; Banerjee 1995; Ravi *et al* 1999), we have included the orthorhombic structure as yet another possible structure for Ti_2ZrAl . There are only three distinctive ways of arranging the Ti, Al and Zr atoms in the orthorhombic structure consistent with the fact that the glide plane parallel to the (1100) plane of DO_{19} structure is retained in the orthorhombic structure. The three possible ways of arranging the atoms are: (i) Zr atoms occupy a distinct sublattice of their own or they occupy a sublattice which was previously associated with Ti atoms, (ii) Zr atoms occupy a distinct sublattice of their own but interchanged with the Al sublattice on the $c/2$ plane and (iii) Zr atoms randomly substitute Ti, or Al or both sites. In such a situation the sublattices remain identical to that of Ti_3Al structure. As the case (iii) represents a disordered alloy, it is not included in the present calculation. The coordinates of atoms in cases (i) and (ii) are the following: (i) Ti(1/4, 1/12, 3/4); Zr(0, 1/3, 3/4); Al(0, 1/6, 1/4); (2) Ti(1/4, 1/3, 3/4); Zr(0, 1/12, 3/4); Al(0, 5/12, 1/4), respectively.

3. Computational details

The total energy calculations were carried out using the tight binding-linear muffin-tin orbital (TB-LMTO) method (Andersen and Jepsen 1984). The conventional LMTO method and its tight-binding versions are well described in the literature (Andersen 1975; Skriver 1984; Horsfield and Bratkovsky 2000). The sphere radii were chosen so as to achieve a good compromise between the sphere overlaps (about 8%) and the proper charge transfer between spheres. The von Barth-Hedin (1972) exchange-correlation potential was used in this calculation. About 340 irreducible k -points have been used for the $B2$ -like, $L1_2$ -like and $L2_1$ structures and about 460 irreducible k -points have been used for DO_{19} -like and the orthorhombic structures. These calculations employ a minimal basis set consisting of s , p and d orbitals for Al and Ti, and s , p , d and f orbitals for Zr atoms. Combined correction terms that correct errors due to overlapping spheres in the atomic sphere approximation have been incorporated in the calculation. The valence states were calculated in a semi-relativistic approximation and the core states were treated fully relativistically. The new version of tetrahedron method has been used for Brillouin zone integration (Blochl *et al* 1994), which avoids improper weighting and also corrects for errors due to the linear approximation of bands inside each tetrahedron. The self-consistency iterations were continued until the total energy difference between two consecutive iterations was less than a microrobydberg.

4. Site preference and ground-state properties

Calculation of the formation energy is carried out to facilitate a comparison of the site preference, phase stability and bonding (Robbins and Falicov 1984; Watson and Weinert 1998). In order to determine the formation energy, we first obtained the total energy of Ti, Zr and Al elements for their respective equilibrium lattice parameters. The difference between total energy of the compound and the concentration-weighted sum of the total energy of the constituent elements gives the heat of formation. The systematic errors in the total energy arising due to atomic sphere approximation get cancelled significantly, leading to a reasonably accurate formation of energy. The total energy of Ti_2ZrAl for each of the 16 inequivalent decorations of $\text{DO}_{19}\text{-Ti}_3\text{Al}$ unit cell (obtained by replacing one of the three Ti atoms with a Zr atom) have been optimized with respect to both the lattice parameters, a and c , simultaneously. Figure 2 gives the total energy as a function of lattice parameters corresponding to decoration 15 given in table 1.

The formation energies along with the relaxed lattice parameters are given in table 1. The relatively large value of heat of formation of decoration 16 establishes the fact that Zr atoms prefer to get substituted at the Ti sites in the DO_{19} structure of Ti_3Al which is in agreement with the experimental report. Any of the decorations where Zr is getting substituted fully or partially in the Al sublattice is found to have significantly less negative heat of formation.

The results of total energy calculations as a function of unit cell volume are presented in figure 3 which can be used for examining the crystal structure stability of Ti_2ZrAl . In table 2 we give the calculated value of lattice parameters, heat of formation (ΔH) and bulk modulus (B_0) of Ti_2ZrAl for the seven structures considered in this

calculation. From the total energy curves (open circle and open box in figure 3) and from the values of heat of formation, this calculation (within the error bars of TB-LMTO method) shows that both DO_{19} -like and L_{12} -like phases are almost degenerate and hence they are competing ground-state structures of Ti_2ZrAl .

The calculated lattice parameters of DO_{19} -like ($a = 10.994$ a.u. and $c = 8.961$ a.u.) and L_{12} -like ($a = 7.748$ a.u.) phases are found to be in good agreement with the experimental values (DO_{19} : $a = 11.265$ a.u. and $c = 9.057$ a.u.; L_{12} : $a = 7.753$ a.u.). The bulk modulus and equilibrium volume were obtained by fitting the total energy as a function of volume to the universal equation of state (Vinet *et al* 1986) for solids under compression. Due to non-availability of experimental values, we could not make a comparison of the calculated heat of formation and bulk modulus (-0.273 eV/atom and 1.410 Mbar for the DO_{19} -like phase). However, these values are found to be comparable to those (Yoo *et al* 1995) of Ti_3Al (-0.26 ± 0.02 eV/atom and 1.30 Mbar).

As stated earlier, Ti_2ZrAl is found (Sornadurai *et al* 2000a) to have the same DO_{19} type crystal structure of parent compound, Ti_3Al , with random replacement of Ti atoms by Zr. The same authors have observed (Sornadurai *et al* 2000b) that Ti_2ZrAl transforms to a cubic (L_{12} structure with a lattice parameter of 7.7535 a.u.) phase under 85 keV Ar^+ irradiation at a dose of 1×10^{17} ions/cm². These experimental findings have to be compared with the results of the present calculation which shows that the total energy of the L_{12} -like structure is lower than that of the DO_{19} -like structure by 0.054 eV. It must also be pointed out that the results of the present calculation are consistent with an earlier first-principles calculation (Zou *et al* 1995) which has shown that Zr is a candidate element for stabilizing the cubic L_{12} structure for Ti_3Al . It should be noted that Ti_2ZrAl

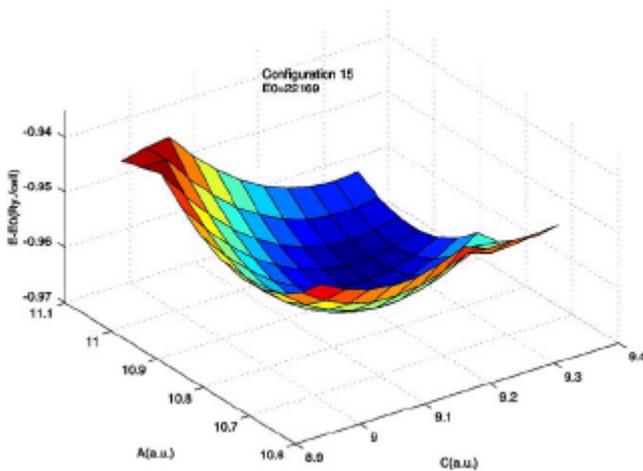


Figure 2. Total energy as a function of lattice parameters corresponding to the decoration 15 (in table 1) for Ti_2ZrAl in the DO_{19} structure of Ti_3Al .

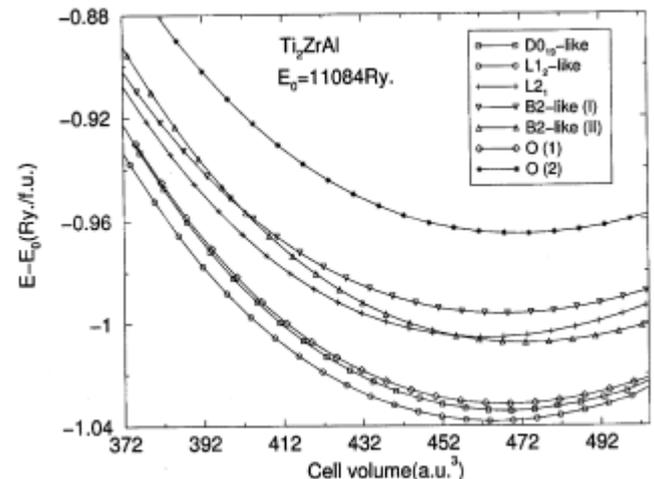


Figure 3. Total energy as a function of unit cell volume of Ti_2ZrAl for the different competing structures considered in this calculation.

Table 2. Ground-state properties of Ti_2ZrAl : theoretical and experimental lattice constants (in a.u.), heat of formation, ΔH (in eV/atom), density of states at the Fermi energy, $N(E_F)$ (in states/Ry/f.u.) and bulk moduli, B_0 (in Mbar).

Structure	a_0	b_0	c_0	ΔH	$N(E_F)$	B_0
DO_{19} -like	10.994		8.961	-0.273	37	1.410
	11.265*		9.057*			
$O(1)$	11.298	18.494	8.978	-0.264	29	1.315
$O(2)$	11.298	18.594	9.027	-0.0386	69	1.100
L_{12} -like	7.748			-0.286	52	1.258
	7.753 [†]					
$B2-I$	6.163			-0.143	78	1.515
$B2-II$	6.182			-0.183	80	1.737
L_{21}	12.267			-0.175	85	1.950

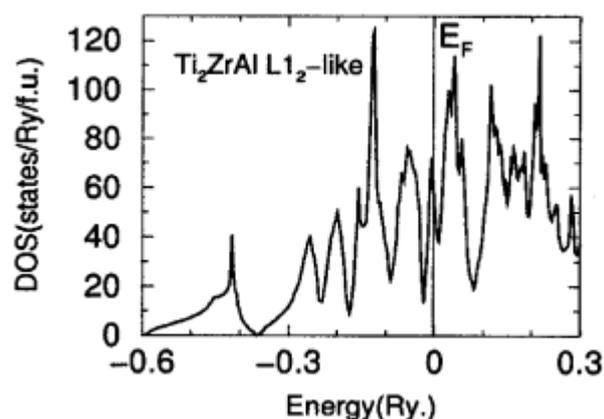
*Sornadurai *et al* (2000a); [†]Sornadurai *et al* (2000b)

was prepared (Sornadurai *et al* 2000a) by arc-melting technique where the synthesis takes place at high temperature and the sample is quenched to a relatively low temperature. If DO_{19} structure has a larger entropy than L_{12} structure, it is possible that free energy of the DO_{19} structure is lower than that of the L_{12} structure at high temperatures, even though the L_{12} structure has a lower internal energy than that of the DO_{19} structure. If that were indeed the case, then Ti_2ZrAl would form in the DO_{19} structure at high temperature and the very same structure would be preserved upon quenching to low temperature. It is plausible that irradiation would provide the necessary energy for the rearrangement of atoms so as to bring about the transition from the DO_{19} phase to the more stable L_{12} phase at low temperature.

The third and seventh (open diamond and star in figure 3) curves correspond to two different site occupations of the Ti, Zr and Al atoms in the ordered ternary orthorhombic structure. The significant energy difference (0.132 Ry) between these two curves indicate that, though both $O(1)$ and $O(2)$ are base-centred orthorhombic structures, site occupancy difference plays an important role in deciding the relative stability of the phases. We also observe that between the two possible site occupancy of atoms in the $B2$ -like structures (triangle-down and triangle-up in figure 3), $B2-II$ (where Zr is substituted in the Ti sublattice) shows enhanced stability, which is in agreement with Banerjee's (1995) report. The energy of the L_{21} structure lies in between that of the two $B2$ -like structures.

5. Density of states

In order to gain more information on the structural stability and bonding of Ti_2ZrAl , we looked at its density of states. In figure 4 we present the density of states of L_{12} -like phase of Ti_2ZrAl , and the total density of states of other structures considered in this calculation are shown in figure 5. In these figures, the Fermi level is taken as the zero of energy. The plots of the density of states

**Figure 4.** Density of states of Ti_2ZrAl for the L_{12} -like structure. Energies are taken relative to the Fermi level, E_F .

reveal a low-lying band at about -0.4 Ry dominated by Al $3s$ states and separated from other bands by a narrow forbidden region that is quite prominent for L_{12} -like, DO_{19} -like, $O(1)$ and L_{21} structures. But, this (pseudo) gap is less prominent in $B2$ -like and $O(2)$ structures. The bands from about -0.34 Ry up to the Fermi level are due to hybridized Ti $3d$, Zr $4d$ and Al $3p$ states with dominant contribution from Ti $3d$ states. The peaks near the Fermi level are due to the Ti $3d$ and Zr $4d$ states. For the L_{12} -like phase, the Fermi level falls at a non-bonding Ti $3d$ state. Moreover, the density of states of Ti_2ZrAl in L_{12} -like and DO_{19} -like structures share a number of common features present in that of (Hong *et al* 1991; Ravindran and Asokamani 1994) Ti_3Al and Zr_3Al . It can be seen that the density of states of Ti_2ZrAl in DO_{19} -like and in $O(1)$ structures have almost similar features. In both DO_{19} -like and $O(1)$ structures we find that the Fermi level lies at a point very close to the pseudogap. The density of states at Fermi level ($N(E_F)$) for DO_{19} -like, $O(1)$ and L_{12} -like structures are 37, 29 and 52 (states/Ry/f.u.), respectively. The correlation (Gelatt *et al* 1983; Hong and Freeman 1991; Paxton 1992) of phase stability to low

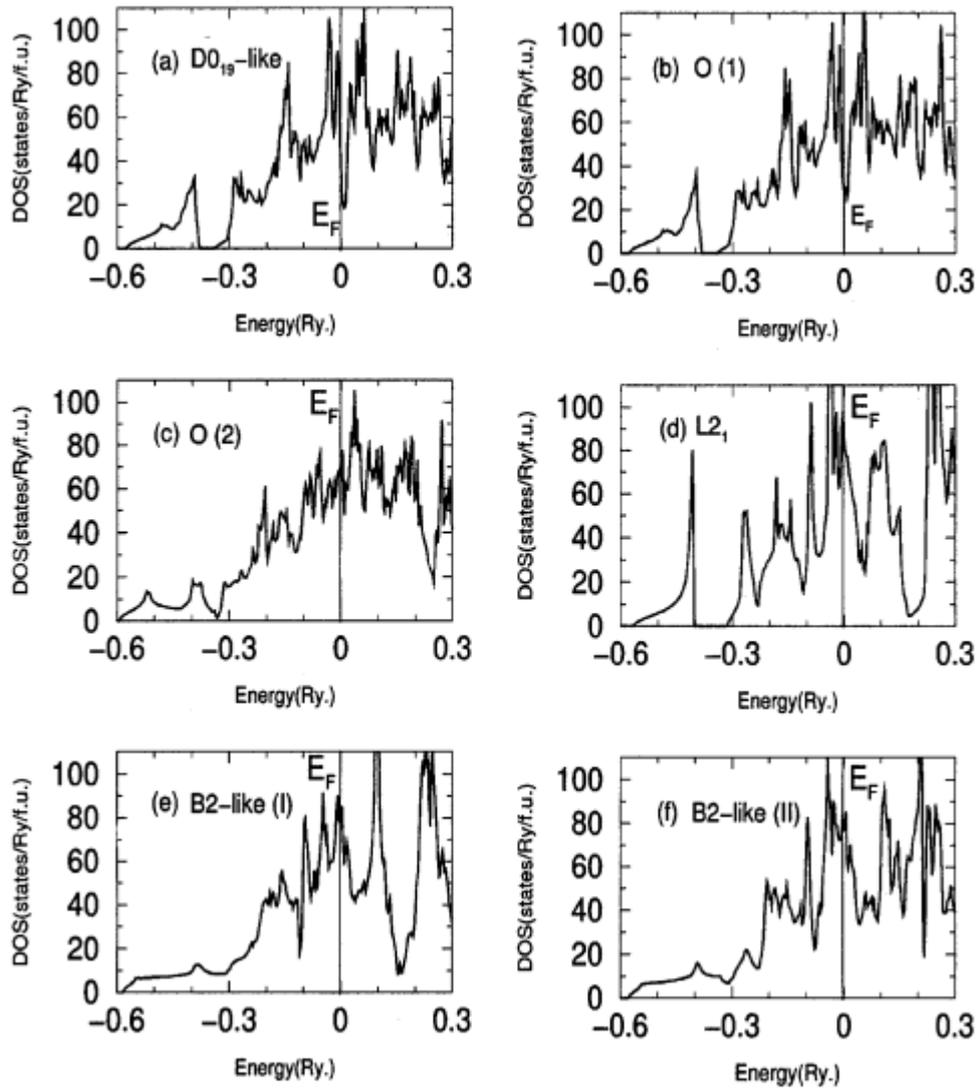


Figure 5. Density of states of Ti_2ZrAl for the $D0_{19}$ -like, $O(1)$, $O(2)$, $L2_1$, $B2$ -like (I), and $B2$ -like (II) structures. Energies are taken relative to the Fermi level, E_F .

$N(E_F)$ and Fermi level falling at the pseudogap is not so obvious from these pictures. This further indicates that the phase stability of Ti_2ZrAl (in $D0_{19}$ -like and $L1_2$ -like structures) is due to a competition between temperature effects and symmetry of the underlying lattices. However, the dependence of phase stability to the shape of the density of states may explain the unstable nature of $B2$ -like, $L2_1$ and $O(2)$ structures, where the pseudogap is absent and Fermi level lies at a peak in the density of states leading to large $N(E_F)$. It may also be noted that even though $O(1)$ and $O(2)$ are base-centred orthorhombic structures, their density of states differ significantly indicating presence or absence of pseudogap at Fermi level is not only controlled by the symmetry of the underlying lattice (Weinert and Watson 1998) but also on the symmetry of the basis atoms.

6. Summary of the results

This calculation clearly shows that Zr additions to $D0_{19}$ - Ti_3Al prefer to get substituted in the Ti sites. Among the seven probable structures considered, we find that both $D0_{19}$ -like and $L1_2$ -like structures are competing ground-states of Ti_2ZrAl . The calculated lattice parameters of Ti_2ZrAl in $D0_{19}$ -like and $L1_2$ -like structures are found to be in good agreement with experimental values. The heat of formation and bulk modulus of $D0_{19}$ -like Ti_2ZrAl are found to be comparable with those of Ti_3Al . Between the two $B2$ -like structures, Ti_2ZrAl shows preference to the one ($B2$ -II) where Zr is substituted in the Ti sublattice. Optimization of total energy by relaxing the lattice parameters for $L1_2$ -like and $B2$ -like structures shows enhanced stability for slight deviation from cubicity. Analysis

of the density of states shows that phase stability need not necessarily follow from the presence of a pseudogap.

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