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Electronic structure of Ti_2AlNb (O phase)

Xiang-Yuan Cui[†], Yang Jinlong^{†||}, Li Qunxiang[†], Xia Shangda[‡] and Wang Chongyu[§]

[†] Open Laboratory of Bond Selective Chemistry and Department of Astronomy and Applied Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China

[‡] Department of Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China

[§] Central Iron and Steel Research Institute, Beijing 100081, People's Republic of China

E-mail: jlyang@ustc.edu.cn

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Abstract. First-principles calculations based on the total-energy, all-electron, full-potential linear muffin-tin orbitals method within the local-density approximation have been employed to study the ground-state properties of the ternary intermetallic Ti_2AlNb (O phase). The equilibrium volume, cohesive energy, formation energy, and bulk modulus are obtained. The results calculated compare well with the available experimental results. The densities of states and charge-density plots show that the bonding in Ti_2AlNb is metallic in nature and has a more covalent bond than in Ti_3Al . It is found that Nb atoms decrease the covalent bonding around themselves locally and increase the degree of directional bonding between Ti and Al, which may explain why Ti_2AlNb (O phase) enjoys better ductility and fracture toughness than Ti_3Al .

1. Introduction

Because of their attractive mechanical, electrical, and magnetic properties, intermetallic compounds have a wide range of applications in different areas and have generated many interesting questions for research [1]. In particular, $\text{Ti}_3\text{Al}(\alpha_2)$ -based titanium aluminides have been the focus of extensive work in the past two decades. The low density of binary Ti_3Al alloys and their ability to retain high stiffness, strength, and creep properties to temperatures up to 760 °C have made them attractive candidates for application as aircraft engine and airframe structural components, in both monolithic and composite forms [2, 3]. In the early years of investigation, alloying additions rapidly became a necessity as, despite its many remarkable properties, Ti_3Al exhibited unacceptably low room-to-intermediate-temperature ductility and fracture toughness [2, 4]. Additions of β -stabilizing elements, and in particular of Nb, appeared to provide a better balance of mechanical properties by allowing the retention of the high-temperature β -phase, or its ordered B2 derivative, at room temperature and by altering the composition of the α_2 -phase [5]. The Ti–24Al–11Nb alloy, first identified by Blackburn *et al* [6], hence became one of the most promising $\alpha_2 + (\beta \text{ or B2})$ Ti–Al–Nb ternary alloys. However, more progress was still needed with some of the poor properties inherent to Ti_3Al -based intermetallics as mentioned above. More complex Ti_3Al -based alloys were

|| Author to whom any correspondence should be addressed.

subsequently developed, such as the super- α_2 Ti–25Al–10Nb–3V–1Mo alloy, with only minor improvements in properties [3].

The recent discovery by Banerjee *et al* [7] of a new ordered orthorhombic (O) phase based on the stoichiometric Ti₂AlNb composition has suggested new directions for property improvement over Ti₃Al-based titanium aluminides. The O phase is structurally very similar to the hexagonal Ti₃Al phase to which it is related by very small distortions [7]. Alloys based on Ti₂AlNb (O phase) appear to exhibit higher room temperature ductility and fracture toughness and room-to-high-temperature (675 °C–750 °C) specific strength compared with $\alpha_2 + (\beta$ or B2) alloys [8]. Additionally, recent studies have shown the benefits of using an O-based alloy relative to using an α_2 -based alloy as a matrix with continuous SiC reinforcement in terms of mechanical properties, both absolute and specific, and of fibre–matrix interfacial reactions [9].

While many efforts have been made to study the O-based alloys in different fields experimentally [10, 11], to our knowledge, no theoretical research on its electronic structure has yet been reported. In this paper, we report a first-principles study on the ground-state properties of Ti₂AlNb (O phase). We describe our computational details in section 2 and present our results and a discussion in section 3. Finally a summary is given in section 4.

2. Computational details

In this paper, a big unit cell (16 atoms) for Ti₂AlNb with a *Cmcm* (D_{4h}^{19}) symmetry [7] is used. Since the atomic bonding in intermetallics generally has both metallic and directional characteristics, a full-potential approach is essential [12]. The calculations presented in this paper were carried out using a full-potential linear muffin-tin orbitals (FP-LMTO) method. This program was developed by Methfessel [13, 14] using the basis set introduced by Anderson [15]. This method divides space into volumes within nonoverlapping muffin-tin spheres plus the surrounding interstitial region. By choosing the muffin-tin radii of 2.66 au for Ti, 2.64 au for Al, and 2.68 au for Nb, we produce a cell that is packed quite well. The interstitial charge density is obtained by matching a linear combination of atom-centred Hankel functions with $\ell \leq 4$ and with two different kinetic energies to the values and slopes of the sphere densities. The ‘tail’ with $\ell > 4$ of the Hankel functions extends into the spheres, so the final density is continuous and smooth, and includes angular momentum terms to infinite ℓ in the spheres. To evaluate the matrix elements of the interstitial potential, the product of two Hankel functions, which represent LMTO envelope functions, is fitted in the interstitial region by a linear combination of Hankel functions in the same way as the charge density. Exchange and correlation were treated in the local-density approximation (LDA) using a form due to Ceperley and Alder [16]. We have used a relatively large basis of 27 LMTOs/atom for Ti, Al, Nb. The convergence of the total energy to within 0.1 mRyd/cell is obtained with the parameters mentioned above.

3. Results and discussion

In order to check the reliability of our computational method and obtain the results for Ti₃Al (α_2 -phase) for comparison in the following subsections, we first study α_2 -Ti₃Al. The computed equilibrium properties are listed in table 1. Our optimized lattice parameters ($a = 10.91$ au and $c/a = 0.8007$) agree well with the experimental values ($a = 10.86$ au and $c/a = 0.8002$) [18]. The calculated formation energy and bulk modulus are 0.27 eV/atom and 1.236 Mbar respectively. They compare well with the corresponding experimental values (0.26–0.29 eV/atom and 1.2 Mbar). Clearly, these results show that our computational scheme

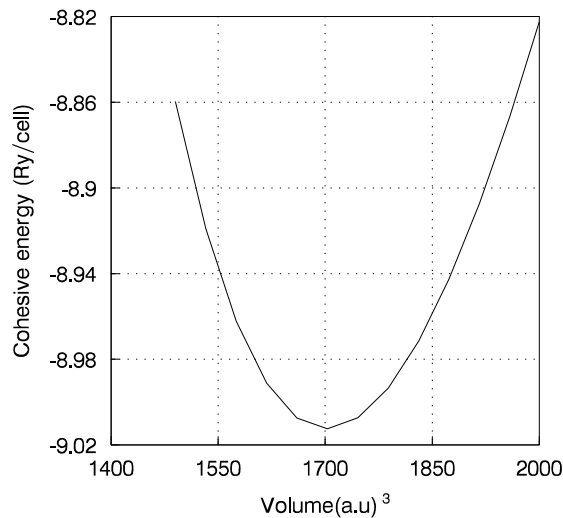
Table 1. The lattice parameters (au), cohesive energy E_{coh} (Ryd/atom), formation energy ΔH (eV/atom), and bulk modulus B (Mbar) of Ti_3Al (α_2) and Ti_2AlNb (O).

	Ti_3Al (α_2)		Ti_2AlNb (O)	
	This work	Experiment [18]	This work	Experiment [10]
Lattice parameters	$a = 10.86$ $c/a = 0.8002$	$a = 10.91$ $c/a = 0.8007$	$a = 11.51$ $b = 18.09$ $c = 8.83$	$a = 11.23$ $b = 17.67$ $c = 8.62$
E_{coh}	0.501		0.563	
ΔH	0.27	0.26–0.29	0.23	
B	1.236	1.2	1.378	> 1.24

is quite reliable. We also obtained the densities of states (DOS) and charge-density distribution of the α_2 - Ti_3Al . They are very similar to those calculated previously using the LMTO method [18].

3.1. Equilibrium properties

Self-consistent total energies are calculated for the ordered Ti_2AlNb (O phase) alloy with the ratios b/a and c/a kept equal to their experimental values (1.57 and 0.768 respectively) [10]. The variation of the cohesive energy with volume per cell exhibits the expected parabolic behaviour as shown in figure 1. Applying a nonlinear least-squares fit for the cohesive energy to Murnaghan's equation of state [17], we obtain the maximum cohesive energy per atom $E_{coh} = 0.563$ Ryd/atom and the corresponding equilibrium cell volume $V = 1702.4$ au³. The calculated value of V is about $0.93V_0$, where V_0 is the experimental cell volume. This error is typical for a calculation using LDA. We also obtain the formation energy from the calculated total-cohesive-energy value of the O phase and that of hcp Ti (0.542 Ryd/atom),

**Figure 1.** Cohesive energy versus volume per cell for Ti_2AlNb . The curve is a least-squares fit to the Murnaghan equation of states (see the text).

bcc Nb (0.805 Ryd/atom), and fcc Al (0.300 Ryd/atom). The calculated formation energy for the O phase is 0.017 Ryd/atom (0.23 eV/atom), which is smaller than that of α_2 -Ti₃Al (0.27 eV/atom). This can be readily understood since Ti₃Al is a stable phase while Ti₂AlNb is a metastable phase. Since there is no experimental or calculated formation energy for the O phase available, our result should provide a helpful point of reference for experimentalists.

The calculated bulk modulus of the O phase is 1.378 Mbar (table 1). Since the bulk modulus was calculated from the second derivative of the total energy versus the volume of the unit cell, a 10–30% error is generally involved [19]. Furthermore, the experimental bulk modulus value for the single-phase alloy Ti–27Al–20Nb is 1.184 Mbar, and that for Ti–27Al–24Nb is 1.230 Mbar. And the bulk modulus of the O phase is found to increase with Nb content [20]. In view of these points, our bulk modulus value for the O phase is quite satisfactory. The calculated bulk modulus of the O phase is larger than that of the Ti₃Al, in accordance with the experimental fact that the O phase enjoys better mechanical properties than the α_2 -phase does. In addition, the fact that the bulk modulus of Ti₂AlNb is larger than that of Ti₃Al indicates that the atomic interaction in the former is stronger. Considering the similarity of atomic occupation of Ti₂AlNb and Ti₃Al, we can say that Nb atoms strengthen the average interaction among constituent atoms.

3.2. Densities of states

The total and three-site DOS of Ti₂AlNb are shown in figure 2. For comparison, we also plot the total DOS of Ti₃Al in figure 2. From figure 2, we can see several remarkable features:

- (1) The hybridization in Ti₂AlNb is found to be fairly strong. In fact, it creates two distinct valleys in the DOS curve (labelled as A and B in figure 2). Valley B (the ‘pseudogap’) is near the Fermi energy E_F and is relatively shallow, but valley A is so deep that it creates or almost creates a semiconductor-like gap in the DOS curve. This feature indicates that the interaction between the constituent atoms is strong and that covalent bonding should exist. Similar phenomena are observed for Ti₃Al and Ni₂XAl ($X = \text{Ti, V, Nb, Hf and Ta}$) [18, 21, 22], but the width of gap A is much narrower there. Below valley A, the DOS are mainly contributed from Al, and above valley A, especially near E_F , the DOS are mainly contributed from Ti and Nb. In fact, the contributions of Al, Ti, and Nb to $N(E_F)$ are 3.7, 18.1, 14.6 states Ryd⁻¹/cell for the O phase, respectively.
- (2) Overall, the bonding and antibonding regions can be roughly separated by valley B. The bonding region is below valley B and the antibonding region is above B. By examining the structure of the DOS curves of Ti₂AlNb and Ti₃Al, one can find that E_F for Ti₃Al lies at a point very close to the bottom of valley B, and 0.12 electrons are needed to accommodate from E_F to the minimum point. For Ti₂AlNb, however, 0.23 electrons have to be released to reach the minimum point from E_F . This feature is again consistent with the fact that the O phase is metastable according to Freidel’s bonding model [23].
- (3) The DOS curves for the Ti and Nb sites are quite similar overall (see figures 2(c) and 2(e)) and quite different from that of Al. This can be understood since the electronegativity, atomic radii, and the position in the periodic table of Ti and Nb are quite similar but different from those of Al. This is consistent with the fact that Nb atoms occupy Ti sites but not Al sites during the formation of the O phase. The difference between the Nb-site DOS and Ti-site DOS near E_F may account for the improvement in mechanical properties from the α_2 -phase to the O phase. This also suggests that Nb atoms play an important role as regards the material’s properties.

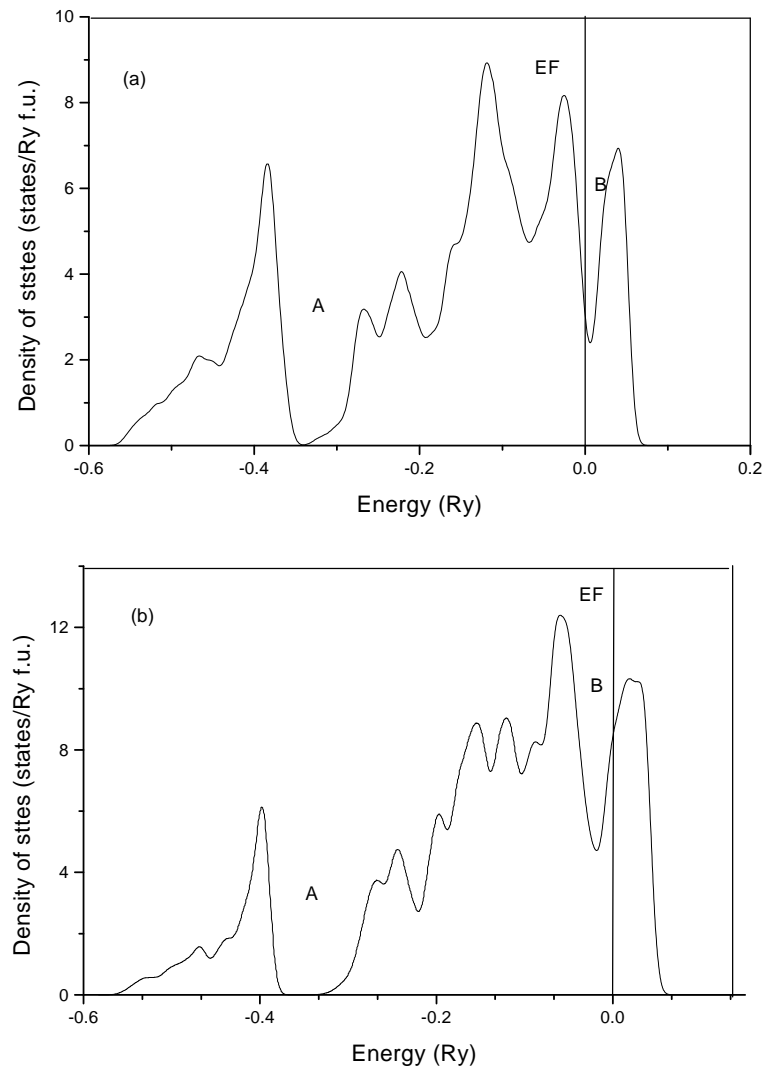


Figure 2. The total DOS for (a) Ti_3Al and (b) Ti_2AlNb , and the site DOS for (c) Ti, (d) Al, and (e) Nb in Ti_2AlNb .

3.3. Charge density

The mechanical strength of materials is ultimately related to the atomic bonding strength. To illustrate the nature of the bonding, we show the valence charge density for the (001) plane of Ti_2AlNb and the (0001) plane of Ti_3Al in figure 3. The atomic arrangements are similar on these two planes except that two Nb atoms substitute for two Ti atoms per cell. By comparing the charge density for the α_2 -phase and the O phase, we stress several characteristics as follows.

- (1) The bonding in the O phase is metallic in nature since the valence charge density is fairly uniform. The same result is predicted experimentally from the unaffected Poisson's ratio while increasing the shear modulus and Young's modulus with the Nb content [20].

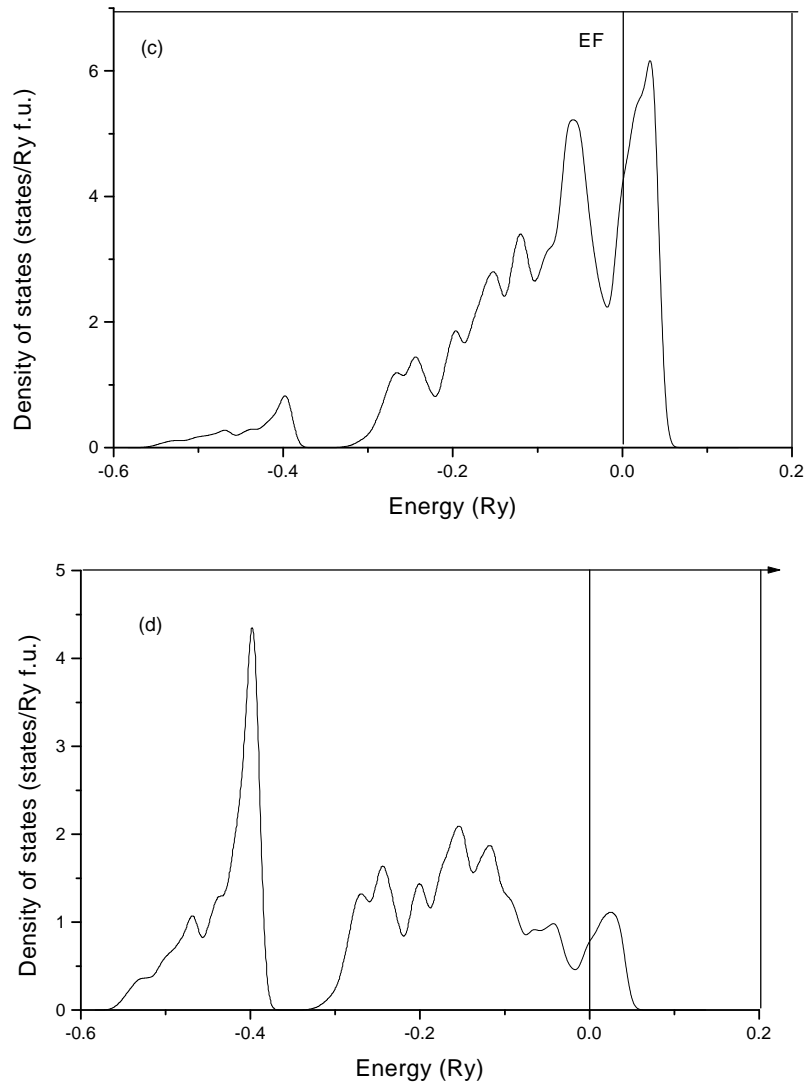


Figure 2. (Continued)

- (2) Corresponding to the analyses of the DOS above, we do indeed find the covalent bond. The charge density is less homogeneously distributed on the (001) plane of the O phase than on the (0001) plane of the α_2 -phase. The charge density around Nb atoms is quite localized, meaning no covalent bonding. But between Al atoms and Ti atoms directional covalent bonding is clear. So, we conclude that the bonding of the O phase is mainly metallic with a small amount of covalency as well. The existence of covalency may contribute to the material's good stiffness.
- (3) In Ti_3Al , the directionality of the bonding is mainly located between Ti atoms. This can be readily seen from the difference charge-density plot [18]. While in Ti_2AlNb , Nb atoms replace part of the Ti atoms, decreasing the covalent bonding around themselves, and increasing the number of directional Ti–Al bonds. It seems that Nb atoms act as ‘axles’

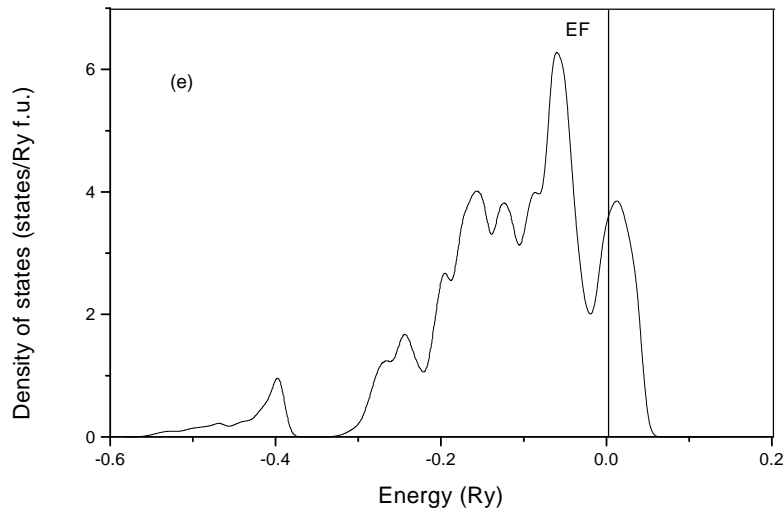


Figure 2. (Continued)

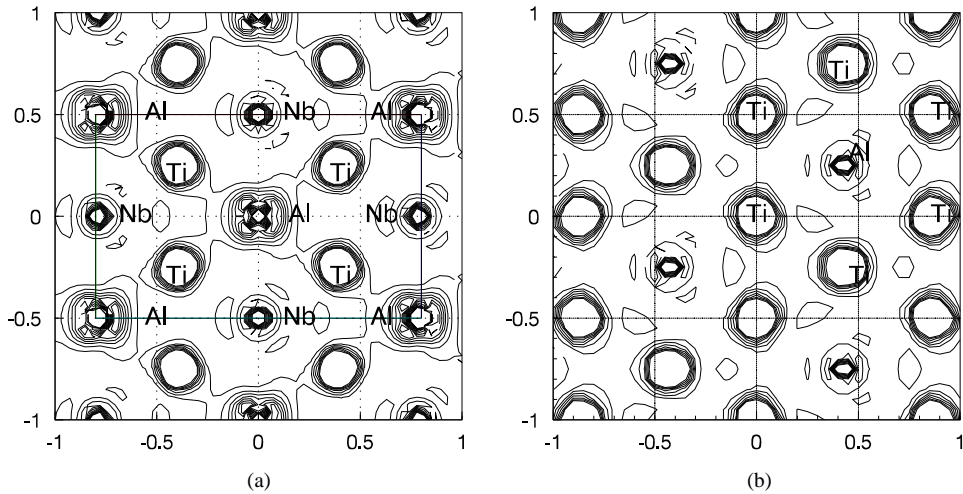


Figure 3. The total valence-electron density for (a) the Ti_2AlNb (001) plane and (b) the Ti_3Al (0001) plane. The increment of the contour step is 10^{-2} electrons au^{-3} . The labelled atoms (in the frame) are in a cell.

in this compound. Although there is more covalency than in Ti_3Al , Ti_2AlNb enjoys much improved ductility and fracture toughness. This may be due to the special contribution of Nb atoms.

4. Summary

In this paper, we have performed a first-principles study on the ground-state properties of Ti_2AlNb (O phase), using the FP-LMTO method. The equilibrium volume, cohesive energy, formation energy, and bulk modulus are obtained. The results calculated compare well with

the available experimental results. The electronic structures of Ti_2AlNb show that the bonding in Ti_2AlNb is metallic in nature and has more covalency than in Ti_3Al , and that Nb atoms decrease the degree of covalent bonding around themselves locally and increase the degree of directional bonding between Ti and Al. Our results may explain the fact that Ti_2AlNb (O phase) enjoys better ductility and fracture toughness than Ti_3Al .

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