First-principles study of $L1_0$ Ti-Al and V-Al alloys

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As a first step towards understanding the reduced embrittlement of $L1_0$ Ti-Al alloys which accompanies the introduction of small concentrations of V, we have determined from first principles, using full-potential linearized–augmented-plane-wave calculations, the equilibrium values of the structural parameters and the associated electronic structure for the stoichiometric ($L1_0$) Ti-Al (tetragonal) compound. Our calculated values of c/a and a are in good agreement with experiment. Using the same method of calculation, we have also studied the electronic structure associated with the (hypothetical) $L1_0$ V-Al alloy that would form when V is substituted for Ti. We find that (1) the electronic structures of these V-Al alloys are relatively insensitive to variations of c/a and a; (2) near the Ti-Al equilibrium geometry, the electronic structures of the V-Al and Ti-Al alloys are very similar; and (3) that a rigid-band model involving substitution of V for Ti can be used to gain a qualitative understanding of the reduction in c/a which accompanies the introduction of small concentrations of V. We relate the reduction in c/a to important changes in the bonding that accompany the occupation of bands immediately above the Fermi level of the stoichiometric Ti-Al compound.

I. INTRODUCTION

The need for improved materials in various technological applications has generated considerable interest in obtaining information about the factors responsible for improving strength and controlling fracture behavior in ordered intermetallic alloys. At the current time, especially for some of the more important aluminide intermetallic compounds (e.g., Ni-Al, Ti-Al, and Nb-Al), very little is known from a fundamental point of view about the underlying physics which governs strength, ductility, and resistance to fracture and thermal failure.

The aluminides, in particular, have many desirable properties (such as low density, high melting temperatures, and high yield strength); but in many cases, they lack ductility. Quite significantly, this fact has prevented them from being used in most of the proposed applications. Because experience has shown that the deformation properties of these compounds depend strongly on crystal structure and elemental composition, which suggests that their electronic structure plays an important role in their lack of ductility, there is strong motivation for understanding the controlling factors of this behavior from a fundamental, microscopic theory of electronic structure.

At the current time, attempts to apply first-principles, microscopic theories, such as the local-density theory, to the problem of understanding the structural behavior and mechanical properties of intermetallic aluminides have focused on three compounds, Ni-Al,[1] Al₃Ni,[1] and Ni₃Al.[1-3] Beyond these pioneering studies, however, very little has been done theoretically to correlate improvements in the strength or ductility of intermetallic aluminide alloys with changes in the associated microscopic electronic structure. The aim of our current work has been to extend this type of theoretical approach to

the problem of correlating changes in the electronic structure of Ti-Al compounds with improvements in ductility.

In particular, for the case of Ti-Al alloys, an important, though poorly understood, potential mechanism for enhancing ductility involves reducing the c/a ratio of the (tetragonal) $L1_0$ Ti-Al-like aluminide structure through alloying with small concentrations of a third element (for example, V, Fe, or Cr). In principle, this process enhances ductility because as the c/a ratio approaches unity, the (D_{4h}) space group of the $L1_0$ lattice (cf. Fig. 1) acquires an additional symmetry (associated with reflections through the face diagonal of the unit cell). The presence of this additional symmetry, in turn, reduces the number of nonvanishing matrix elements associated with deformation-induced changes in the potential, and the lattice becomes more tensile. Because the c/a ratio is 1.02 Å for stoichiometric $L1_0$ Ti-Al,[4-6] only a small reduction ($\sim 2\%$) in the ratio is required. This feature, in fact, has been identified recently by Blackburn and Smith,[7] who obtained 2% tensile elongation in the a direction after adding small concentrations of V to Ti-Al alloys at temperatures below 260 °C. From a theoretical point of view, however, no attempt has been made to gain a fundamental understanding of this behavior from a microscopic theory of electronic structure. Even for the case of the stoichiometric $L1_0$ Ti-Al, whose structure and composition has been well documented,[4-6] no theoretical investigation of this type has been carried out.

In this paper, we examine results from our first-principles study of the electronic structure of the stoichiometric $L1_0$ Ti-Al alloy. This includes determinations of the equilibrium structural parameters, c and a (cf. Fig. 1), various elastic moduli, and electronic structure. Also, as a first step towards understanding the impact of alloying with V, we have investigated the electronic
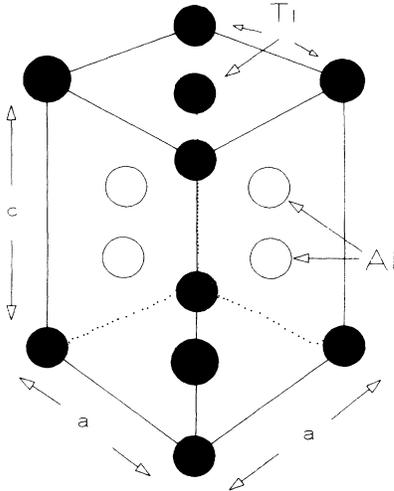
FIG. 1. Structure of $L1_0$ Ti-Al.

structure of the hypothetical V-Al alloy, possessing the same $L1_0$ structure, for various choices of a and c/a. Our detailed electronic structure calculations reveal several striking similarities between the electronic structures of the V-Al and Ti-Al compounds. These similarities suggest that the V-Ti-Al alloy, near the stoichiometric Ti-Al phase, is well described by a rigid bandlike model, in which the reduction in the c/a ratio can be related to a rigid shift of bonding features associated with unoccupied (occupied) Ti (V) -like states located near the Fermi level E_F. Furthermore, as we will show, the electron density associated with the energy bands immediately above E_F in the stoichiometric Ti-Al compound is distributed primarily around and between Ti (or V) atoms located in *different* $\langle 001 \rangle$ planes, while the states below E_F are primarily localized around and between Ti (or V) atoms located in the *same* $\langle 001 \rangle$ plane. Therefore, within a rigid-band framework, the occupation of the states immediately above E_F can be identified with enhanced bonding in the c direction for fixed a values, and a reduced c/a ratio.

II. TOTAL ENERGY AND ELECTRONIC STRUCTURE

We have determined the equilibrium structural parameters of $L1_0$ Ti-Al alloys using the bulk, full-potential linearized–augmented-plane-wave (FLAPW) method as implemented by Wei and Krakauer.[8] This procedure is known to provide accurate total energies and electronic structures. Independent, fully self-consistent calculations of the electronic structure and total energy of the $L1_0$ Ti-Al alloy for 12 different geometries, involving different values of c and a, were performed using 40 special k points. We found that this choice of k-point sampling provided satisfactory convergence of the total energy with respect to changes in geometry by performing eight additional, self-consistent calculations involving alternative k-point meshes (defined by 18, 80, 126, and 160 special k values) for the two geometries defined by $c/a = 1.00$ and $c/a = 1.02$, with $a = 3.99$ Å. As men-

tioned in the Introduction, we also performed comparable calculations of the electronic structure of the hypothetical $L1_0$ V-Al alloy for several values of c and a.

The results of the total-energy minimization for the Ti-Al alloys are shown in Fig. 2. Here we have plotted the total energy and the associated parabolic fit as the c/a ratio is varied for each of four different values of a. We have calculated from separate polynomial fits to our total energies for different values of a, with c/a set equal to 1.02 and 1.00, that the equilibrium Ti-Al a value should be $\sim 3.94(2)$ Å. This value is slightly smaller (by $\sim 1.3\%$) than the experimental result (3.99 Å) due to Bumps et al.[4] The minimum in the fits to the total energies derived with $a = 3.91$ and 3.95 Å occurs when $c/a = 1.03$ and 1.01, respectively. From this, we calculate that the equilibrium c/a ratio is $\sim 1.02(1)$. This result also agrees well with the measured value 1.02 due to Bumps et al.[4] It is quite possible that the small difference between the measured and calculated values of a are due to finite temperature effects, since our results correspond to $T = 0$, and the experimental measurements were made at temperatures above 500 K. Indeed, the values and error specifications given by Valencia et al.[9] for their measured a value [3.99(2) Å] and c value [4.06(2) Å] at room temperature further confirm this possibility.

Our calculated total energy values at $a = 3.91$, 3.95, and 3.99 Å for various values of c also allow us to make the first estimates of various elastic moduli associated with $L1_0$ Ti-Al. In particular, we predict that $C_{13} = 2.01(6)$ Mb, $C_{33} = 1.95(9)$ Mb, and $C_{11} + C_{12}$
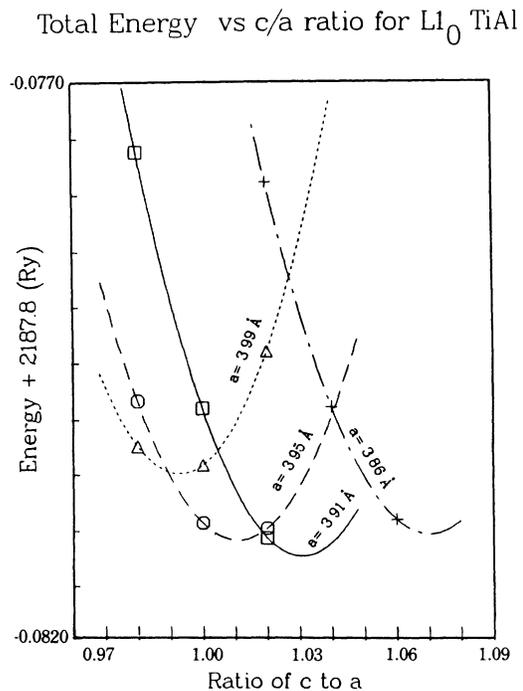
Total Energy vs c/a ratio for $L1_0$ TiAl

FIG. 2. Total energy of $L1_0$ Ti-Al vs the c/a ratio for the four values of a: 3.99 Å (triangles), 3.95 Å (circles), 3.91 Å (squares), and 3.86 Å (crosses), and the polynomial fit to the data for each value of a. Respectively, our calculated equilibrium values of c/a and a are 1.02(1) and 3.94(2) Å.

$= 5.8(4)$ Mb. Independent experimental verification of these values could provide an important test of the accuracy of our calculations.

Using the smooth-fitting procedure developed by Koelling and Wood,[10] we have extrapolated energies from our 40 special k-point mesh to one involving 410 k points. From these extrapolated values, we have used the triangulation package developed by Wang[11] to evaluate the density of states (DOS) for both Ti-Al and V-Al using the values $a = 3.91$ Å, $c/a = 1.02$. This choice of structural parameters occurs very near the equilibrium Ti-Al geometry.

In Fig. 3 we have plotted the l-decomposed, partial DOS and total DOS for the Ti-Al (a) and V-Al (b) cases. In each case, we find a broad, sp-like, bonding band, beginning at about -9 eV (all energies are relative to E_F), which remains primarily delocalized, except near -5 eV, where small, though noticeable peaks on both the Al and transition-metal sites occur in both alloys. The location of this peak, the position and width of the associated sp band, its angular momentum decomposition, and even its shape are essentially the same in both alloys for all energies below ~ -3 eV. Also, in both cases, the transition metal contributes only a very small s component throughout the occupied spectrum, while essentially

equal amounts of s and p component are introduced by the Al.

The most important differences between the Ti-Al and V-Al alloys involve the positions and the occupation of their respective d bands. In particular, in Fig. 3(b), we have used an arrow to show the energy which, in the rigid band sense, is associated with the occupation of the first additional electron (at ~ 0.58 eV) above E_F in the Ti-Al alloy. When we align E_F of V-Al with this energy, we find that the bottom of the Ti-Al d bands and the two lowest Ti (d)-like peaks are shifted slightly (by ~ 0.2 eV) downward relative to the corresponding portions of the V-Al spectrum. In addition, the two lowest Ti (d)-like peaks are slightly broader than their counterparts in V-Al though the similarity in shape and positioning of these peaks and the remaining transition-metal d-band peaks in both alloys is a striking feature of these plots of the DOS. Beginning at the energy corresponding to the occupation of six electrons in both alloys (corresponding to ~ -0.56 eV relative to E_F of Ti-Al) and continuing beyond the energy, 0.58 eV, associated with occupation of eight electrons, the positions, widths, and shape of the peaks and valleys in the DOS's of both Ti-Al and V-Al are virtually indistinguishable. This similarity is quantified further by comparing the values of the total DOS for both alloys at the energies associated with the occupation [number of states (NOS)] of six, seven, and eight electrons.[12] In particular, the value of the associated DOS at the energy corresponding to each of these occupations is uniformly reduced (by $\sim 25\%$) in the Ti-Al alloy relative to V-Al. The resulting difference in value (~ 0.53 states/eV unit cell for NOS equal to both 6 and 7 and ~ 0.26 states/eV unit cell when NOS is 8) is systematic and is smallest in the region corresponding to the first unoccupied state above the Ti-Al Fermi energy.

The overall similarity between the DOS of the two alloys (especially in the energy range associated with the addition or removal of one electron from the Ti-Al) suggests that (1) the result of alloying with small amounts of V involves substitution of V for Ti predominantly (and not V for Al), and (2) the reduction in c/a, at least qualitatively, can be understood within the framework of a rigid-band-like model. In this context, by rigid-band-like model we are referring to the approximation in which changes in electronic structure associated with the substitution of V for Ti are described by the occupation of the same number of states immediately above E_F in the stoichiometric Ti-Al alloy. Though such a model might seem crude, it should be noted that only a small concentration of V is involved. Thus, only a small number of states above E_F are assumed to be filled during the alloying process. Hence, our omission of induced charge transfers that go beyond such a description involves only a rather small amount of charge. Also, we have found additional supporting evidence for the credibility of such a rigid-band-like model by examining the dependence of the V-Al DOS on the choice of structural parameters. In particular, over a fairly wide range of a and c values, we found rather minor changes in the DOS, involving shifts of the more tightly bound, lower-energy states, primarily, and very little modification in the spectrum near E_F.[12]
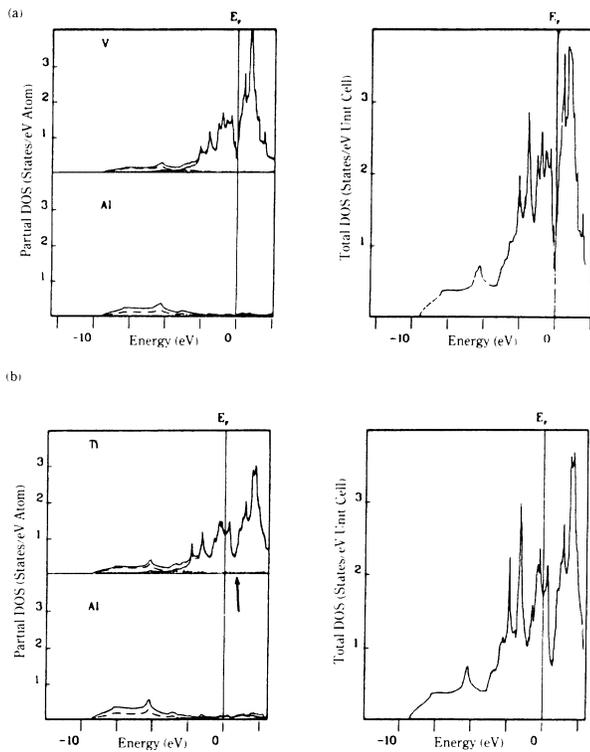

FIG. 3. Partial, l-decomposed DOS for each muffin tin (left) and total DOS for $L1_0$ Ti-Al (a) and $L1_0$ V-Al (b) with $a = 3.91$ Å, $c/a = 1.02$. These values of a and c/a are very close to the equilibrium values, as discussed in the text. In each plot of the partial DOS dotted, dashed, and solid lines are used to distinguish between s, p, and d contributions, respectively. The sum of s, p, and d contributions is also marked by solid lines.

In fact, by assuming that such a rigid-band-like model is valid, we have obtained a qualitative understanding of the accompanying reduction in c/a value directly by examining the orbital character of the states immediately above and below E_F in the Ti-Al alloy, which we now discuss.

In Fig. 4 we have plotted the logarithm of the spectrally and spatially resolved electron density $n(\Delta E, r)$ in the $\langle 100 \rangle$ plane associated with the sum of all single-particle eigenstate densities within specific energy ranges ΔE just above and below the Ti-Al Fermi level. We have constructed these plots, using

$$n(\Delta E, r) = \sum_k \psi^*_{\varepsilon(k)}(r)\psi_{\varepsilon(k)}(r) , \qquad (1)$$

where we have restricted the sum over eigenvalues $\varepsilon(k)$ to the particular energy range, ΔE. Figures 4(a) and 4(c) show the plot of $\log_{10}[n(\Delta E, r)]$ for the choice of ΔE associated with the occupation of the seventh valence electron in Ti-Al and V-Al, respectively.

Because the valences of V, Ti, and Al are five, four, and three, respectively, these plots show the distribution of charge associated with the last (second-to-last) occupied electron of Ti-Al (V-Al). In Figs. 4(b) and 4(d) we show comparable plots of $\log_{10}[n(\Delta E, r)]$ for the range of energies ΔE associated with the occupation of the next highest (eighth) valence electron in the Ti-Al and V-Al alloys. Comparison between Figs. 4(a),4(b) and 4(c),4(d) re-
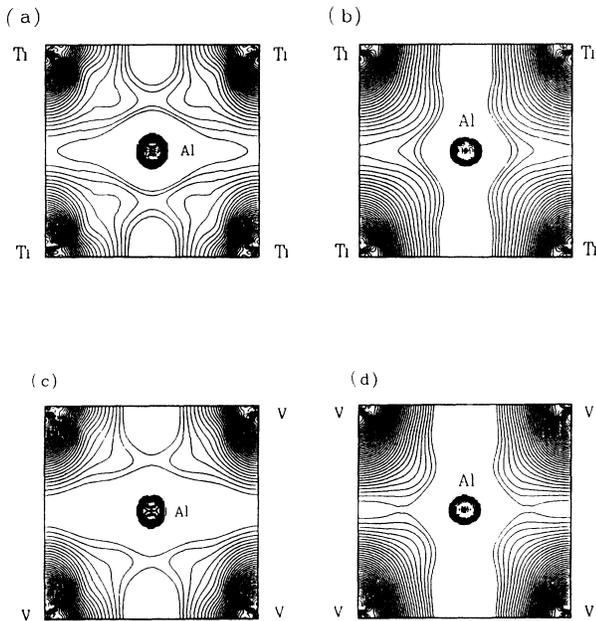
veals that indeed the orbital character and the spatial distribution associated with the states from comparable portions of the Ti-Al and V-Al spectrum, immediately below (above) the E_F of Ti-Al are quite similar. (This fact provides additional support for our use of a rigid-band-like model.) A striking feature of Figs. 4(a) and 4(c) is the absence (accumulation) of appreciable charge within each $\langle 001 \rangle$ plane containing Al (transition metal) atoms. This characteristic of the electron density indicates that the states in both the V-Al and Ti-Al compounds associated with energies just below E_F in the Ti-Al alloy have predominantly transition-metal character and *possess a distinct* d_{xy,x^2-y^2} *character* within the horizontal planes containing transition-metal atoms (see Fig. 1). Thus, the associated electronic states exhibit a tendency towards bonding between transition metal atoms within each $\langle 001 \rangle$ plane and a lack of bonding in the vertical directions away from these planes (either towards the Al atoms or towards transition metal atoms located along the c axis). On the other hand, Figs. 4(c) and 4(d) reveal that comparable states associated with energies just above the Ti-Al Fermi energy from the two compounds possess a distinct $d_{3z^2-r^2}$-like orbital character between transition-metal atoms in different $\langle 001 \rangle$ planes, indicating a tendency towards bonding between transition metal atoms in the direction of the c axis. Thus, if the introduction of V leads to an essentially rigid-band–filling effect, in which the unoccupied states just above E_F in the Ti-Al alloy become occupied as the concentration of V is increased, the presence of V appears to introduce an increased out-of-plane bonding component. This means that as the concentration of V is increased, the c/a ratio will decrease, which is the phenomenon that is observed. This qualitative argument demonstrates that the reduction in the c/a ratio can be inferred from the rigid-band-like nature of the electronic structure. It is a consequence of the greater bonding along the c axis that accompanies the occupation of the unoccupied (occupied) states immediately above (below) E_F in the Ti (V) -Al alloy.

It is also interesting to note that these changes in the orbital character of states near the Ti-Al Fermi level can be related directly to (1) the number of occupied d electrons in the two compounds, and (2) through a tight-binding-like argument, to the geometry of the $L1_0$ structure. In particular, we find that the transition metal primarily contributes d states, and, in both alloys, the Al contributes essentially the same amount of (sp) charge. The valence of Ti is four, while V has five electrons. If most of the transition-metal charge is d-like, then the Ti would possess occupied states involving four d states, while V has occupation from five d states. Each d-like energy band is doubly occupied of course. But the most tightly bound d bands arise from cases involving the shortest transition-metal separations. These are in-plane. Thus, there are two such sets of bonding orbitals, involving d_{xy,x^2-y^2}-like bands, which, in the idealization of negligible s charge arising from the transition metal, and vanishing out-of-plane hybridization with the Al would be the entire source of Ti-like electrons in the Ti-Al alloy.

FIG. 4. The logarithm (base 10) of the spatial distribution of charge (in units of $e/\text{a.u.}^3$) in the $\langle 100 \rangle$ plane for the last (seventh) occupied electron of $L1_0$ Ti-Al (a), the first unoccupied electron above E_F (corresponding to the eighth electron) of the same compound (b), the second to last (seventh) occupied electron of $L1_0$ V-Al (c), and the last (eighth) occupied electron of this V-Al compound (d). Contours are separated by increments of 0.05. The smallest contour corresponds to the value $10^{-2.9}$ $e/\text{a.u.}^3$ of the density.

In fact, out-of-plane overlap does occur, but the inherent ordering of levels should be in-plane, followed by out-of-plane, with the weakest Ti-Ti bonding involving Ti $d_{3z^2-r^2}$-like orbitals. As a consequence, we are able to infer, on the basis of the geometry and the number of occupied transition metal d states, that states possessing primarily out-of-plane (in-plane) orbital character should be positioned just above (below) E_F in the Ti (V) -Al alloy. This conclusion of course is consistent with the presence of out-of-plane orbital character that we have associated with the first (last) unoccupied (occupied) Ti (V) -Al electron [cf. Figs. 4(b) and 4(d)].

Finally, we point out that various features of our rigid-band-like model can be tested by experiment. In particular, directly above E_F in the Ti-Al compound, the DOS rises until it reaches a local maximum at about 0.25 eV and then falls dramatically. In a rigid-band picture, as a consequence, we would anticipate increases both in the angle-integrated photoemission intensity at E_F and in the value of the specific heat as small concentrations of V are alloyed with Ti-Al. Though there have been recent measurements of the specific heat for Ti-rich V-Ti-Al alloys,[13] no measurements of this quantity near the stoichiometric Ti-Al phase have been performed. Also, there have been no photoemission spectrum measurements of V-Ti-Al.

III. CONCLUSIONS

As a first step towards understanding the reduction in c/a ratio that accompanies the introduction of small concentrations of V into Ti-Al alloys, we have determined the equilibrium structural parameters of the $L1_0$ Ti-Al intermetallic alloy, and they are in good agreement with experiment. We have also performed calculations of the electronic structure of the hypothetical V-Al alloy of the same structure from first principles. By comparing the electronic structures of the two alloys, we have identified an important rigid-band-like behavior involving the Ti and V electrons. These results suggest that in the Ti-Al-V alloy, the V probably is substituted for Ti. We have also shown that the underlying mechanism responsible for the reduction in c/a can be directly related to the occupation (and the associated bonding nature) of the new states near E_F that accompanies this V for Ti substitution.

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