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This paper will describe the interplay between the electronic structure and structural energetics in simple, complex, and quasicrystalline Al-transition metal (T) intermetallics. The first example is the  $L1_2$ - $DO_{22}$  competition in  $Al_3T$  compounds. *Ab-initio* electronic total-energy calculations reveal surprisingly large structural-energy differences, and show that the phase stability of both stoichiometric and ternary-substituted compounds correlates closely with a quasigap in the electronic density of states (DOS). Secondly, *ab-initio* calculations for the structural stability of the icosahedrally based  $Al_{12}W$  structure reveal similar quasigap effects, and provide a simple physical explanation for the stability of the complex aluminide structures. Finally, parametrized tight-binding model calculations for the Al-Mn quasicrystal reveal a large spread in the local Mn DOS behavior, and support a two-site model for the quasicrystal's magnetic behavior.

## 1. Introduction

The alloying of aluminum with transition metals is a well-established procedure for producing light, hard materials. Aluminum by itself is light, but soft; even small amounts of transition metals can greatly increase the hardness. More recently, aluminum-transition metal compounds, or aluminides, have been under intensive investigation as possible advanced high-temperature materials. When transition metals are introduced into aluminum, several scenarios are possible:

- 1) A solid solution is formed. This happens only for low transition metal concentrations, as the solid solubility of transition metals in aluminum is low.
- 2) A simple intermetallic compound is formed. These are usually based on the Al fcc structure. They typically have high melting points.
- 3) A complex intermetallic compound is formed. These have many atoms per unit cell, and often display local icosahedral coordination.
- 4) A quasicrystal is formed. In binary Al-transition metal compounds, these are always metastable phases; however, some ternary quasicrystals are stable.

We will consider numerical calculations of the electronic structure of some examples from each of the categories 2), 3), and 4). We will not discuss the solid solutions here; see, however, Ref. 1.

## 2. Basic Principles of Electronic Structure and Structural Stability

The simplest picture of the electronic density of states (DOS) of a transition metal immersed in Al is that the atomic d-levels are broadened into a resonance of finite width by

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interaction with the Al free-electron type states. The d-resonance is typically partly filled. Thus a larger d-resonance width should lead to greater stability, since the average electronic energy is lowered. One also expects, in general, that a broad d-resonance should reduce the likelihood of magnetic-moment formation.

However, the width of the d-resonance is not the only crucial parameter relevant for structural stability. The presence of a gap or quasigap in the DOS around the Fermi level can have very important stabilizing effects. To see this, it is convenient (and legitimate<sup>2</sup>) to compare two bands having the same mean-square width  $\mu_2$ , as defined by the average of  $E^2$  relative to the center of the band. The DOS distributions indicated in Figs. 1a and 1b both have  $\mu_2 = W^2/3$ . The average electronic energy of the gapless DOS is clearly  $-W/2$ . A simple calculation shows that the average energy for the DOS with a gap is  $-W/2 - E_g/8$ , which corresponds to greater stability. Similar results are found for many other forms of model DOS distributions.

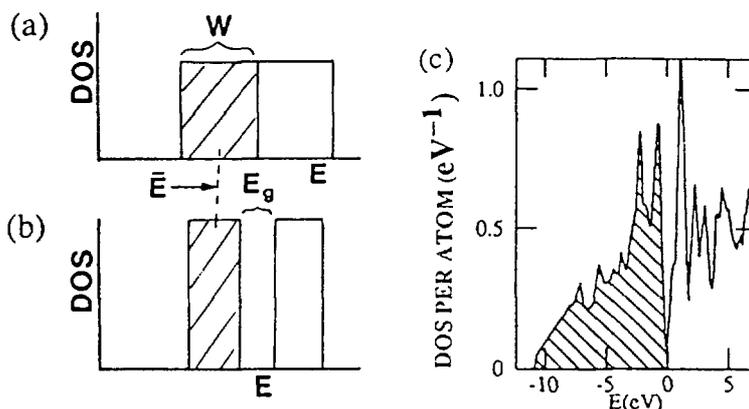


Figure 1. (a) and (b) Model DOS distributions for d-band of transition metal.  
(c) DOS of  $\text{Al}_3\text{Nb}$ , taken from Ref. 4.

### 3. Simple Intermetallics

Here, we consider the competition between the  $L1_2$  and  $DO_{22}$  structures in  $\text{Al}_3T$  compounds. These structures are both based on an underlying fcc structure, on which the transition-metal atoms form different ordered patterns.<sup>3</sup> The  $L1_2$ , or  $\text{Cu}_3\text{Au}$ , structure, has the transition metals in a simple cubic arrangement. In the  $DO_{22}$  or  $\text{Al}_3\text{Ti}$  structure, planes of transition metals atom are shifted laterally so that a tetragonal structure is formed. In possible aerospace applications, it is generally felt that the cubic  $L1_2$  structure has the greatest chance of having desirable mechanical properties.

*Ab-initio* electronic structural-stability calculations have been performed,<sup>4,5</sup> for these structures using both the augmented-spherical-wave<sup>6,7</sup> (ASW) and linear muffin-tin orbital (LMTO) methods; we will discuss the former here. Figure 2 shows the energy difference between the  $DO_{22}$  and  $L1_2$  structures for the Group III, IV, and V transition metals. All of the results shown here are consistent with experiment;<sup>3</sup>  $\text{Al}_3\text{Sc}$  and  $\text{Al}_3\text{Y}$  both form the  $L1_2$  structure (in the latter case only at high temperatures); all of the Group V trialuminides form the  $DO_{22}$  structure. In the Group IV trialuminides, the energetic competition is the most delicate, and another ( $DO_{23}$ ) structure comes into play. The stability of the latter was not always obtained correctly.

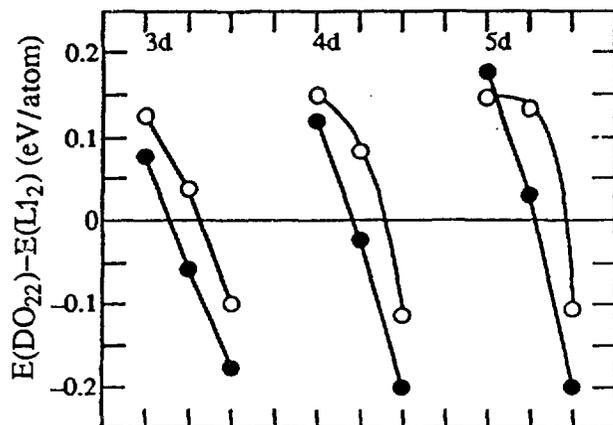


Figure 2. Structural-energy differences for  $\text{Al}_3\text{T}$  compounds, taken from Ref. 4. Open circles indicate results for ideal  $c/a$  ratio in  $\text{DO}_{22}$  structure; filled-circle results have observed or hypothesized  $c/a$  ratios.

Two aspects of Fig. 2 are particularly notable. First, the structural-energy differences vary in a systematic fashion with  $d$ -electron count, in a way that is quite similar from row to row of the periodic table. This suggests that electronic-band effects are the primary mechanism determining the structural stability. This contention is further supported by Fig. 1c, which shows that  $\text{Al}_3\text{Nb}$  has quasigap around the Fermi level. For all of the trialuminides, such feature is found; in light of the preceding discussion, this is expected to lead to structural stability. Second, the scale of the structural energies is quite large. In the Group-V trialuminides, the energy difference is roughly 0.2 eV per atom. Given that the transition-metal environments differ only at the second-neighbor level, this is a remarkably large energy. The Group-IV elements are crossover cases for which the structural-energy differences are the smallest; these should be the most susceptible to structural transformations induced by, for example, ternary additions.

For the purposes of atomistic simulation studies, it is desirable to have descriptions of these types of phenomena via  $r$ -space interaction potentials (*cf.* Fig. 3). These are obtained<sup>8</sup> by simply calculating the total energy of a system of two transition-metal atoms in a uniform electron gas. The potentials display the types of oscillations that are typically associated with metallic screening. As one goes from Sc to Ti, one sees that the first minimum in  $V_2^{\text{eff}}(r)$  moves to shorter separations. This leads to a relative stabilization of the  $\text{DO}_{22}$  structure, in which the second shell of transition-metal neighbors is closer than in the  $\text{L}_{12}$  structure. Such potentials obtain the correct chemical trends in the structural stability, and obtain quite accurate estimates of the structural-energy differences for the Group-V aluminides. It is gratifying that electronic effects can be expressed, at least in an approximate fashion, in terms of pair interaction energies.

Calculations of the effect of ternary additions on structural stability<sup>9,10</sup> were motivated by experimental observations<sup>11</sup> that such additions can stabilize the  $\text{L}_{12}$  structure. The effect of Fe impurities in  $\text{Al}_3\text{Ti}$ , shown in Fig. 4, is approximated by the use of an artificially ordered "supercell" lattice of Fe atoms substituting for Al. It was only possible to treat supercells having up to eight atoms, which corresponds to a 12.5% Fe impurity concentration. The addition of Fe dramatically changes the structural energetics: Interpolation of the results would suggest a crossover to the  $\text{L}_{12}$  structure at around 5% Fe. This is consistent with the observed ternary phase diagram, which has a two-phase field containing the  $\text{L}_{12}$  and  $\text{DO}_{22}$  structures centered at roughly 5% Fe. Parallel calculations were performed for  $\text{Al}_3\text{Nb}$ , which indicated that much greater (and impractical) impurity concentrations would be required to stabilize the  $\text{L}_{12}$  structure in this system.

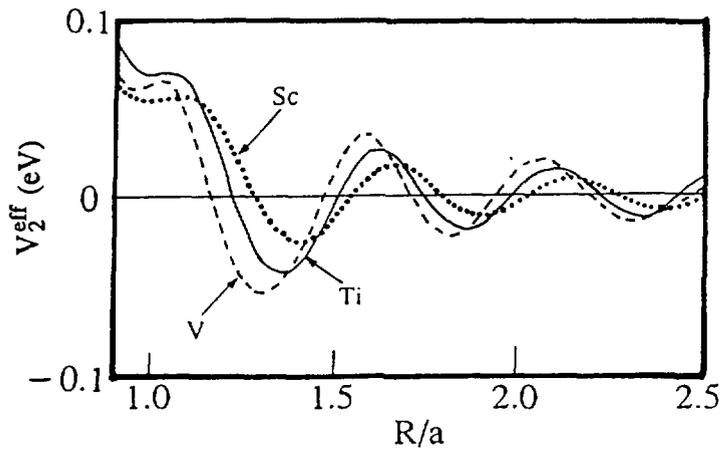


Figure 3. Effective pair potentials for interacting transition-metal impurities in Al, taken from Ref. 8. On abscissa, "a" is cubic lattice constant.

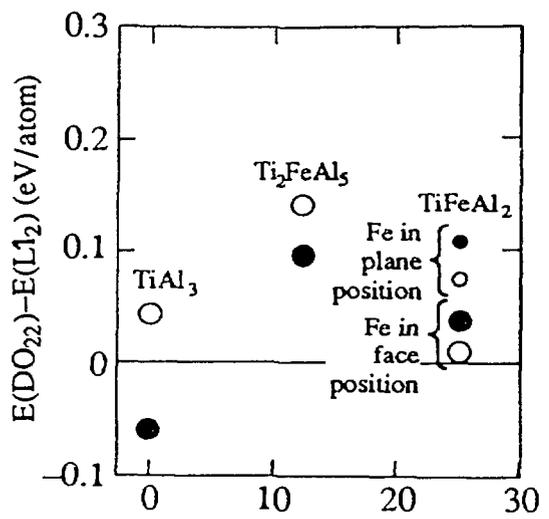


Figure 4. Effect of Fe substitution on structural energies in  $Al_3Ti$ , taken from Ref. 9. Horizontal axis is percent Fe concentration.

#### 4. Complex Structures

The example we consider here is the  $Al_{12}W$  structure,<sup>3</sup> whose basic building block is an icosahedron of twelve Al atoms centered by a transition metal atom. These icosahedra are arranged in a bcc structure, so that each primitive unit cell contains thirteen atoms. The energy of this structure was compared<sup>12</sup> to that of a reference system defined by a combination of a (sometimes hypothetical)  $L_{12}$ -structure  $Al_3T$  compound and fcc Al; this reference system was taken as a representative of simple structures that could be competing with the  $Al_{12}W$  structure.

The main features of the structural-energy results are as follows. First, the  $Al_{12}W$  structure is most strongly favored for nearly half-filled d-bands; for nearly filled or empty d-bands, the  $L_{12}$  structure becomes favored. This is consistent with the experimental observation that the  $Al_{12}W$  structure forms only for nearly half-filled d-bands. The scale of the energies is quite large, on the order of 0.15 eV/atom in the maximal cases. Quasigap effects are again crucial. Figure 5 shows DOS distributions for  $Al_{12}Mn$  and  $L_{12}$ -structure  $Al_3Mn$ . As is seen in the figure, the stable  $Al_{12}Mn$  compound has a quasigap around the Fermi level, while the  $Al_3Mn$  compound has just the opposite: a peak. Comparison of the structural-energy differences with the transition-metal atomic sizes showed a rather poor correlation; a much better correlation was obtained with the position of the Fermi level relative to the minimum of the DOS in the quasigap.

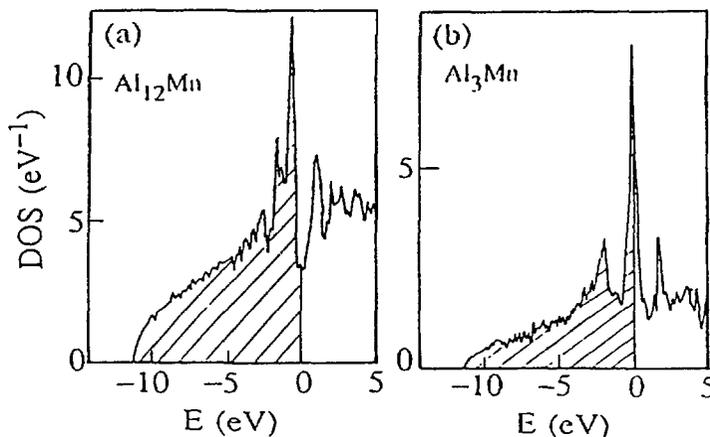


Figure 5. Electron DOS distributions for (a)  $\text{Al}_{12}\text{Mn}$  and (b)  $\text{Al}_3\text{Mn}$ , per unit cell, taken from Ref. 12.

## 5. Quasicrystals

Here we consider the magnetic properties of the Al–Mn quasicrystal, the first to be discovered. The composition is roughly  $\text{Al}_{80}\text{Mn}_{20}$ , and can be varied by roughly 5%. The quasicrystal is obtained by rapid quenching of Al–Mn melts (usually with some Si present as well), and is metastable but not stable. For this reason, and because of the lack of an adequate methodology, we do not calculate structural-energy differences, but focus on calculations<sup>13</sup> of the effects of the DOS distribution on the magnetic properties. Magnetic susceptibility and nuclear-magnetic resonance measurements have indicated that the moment per Mn atom increases with the Mn concentration.<sup>14</sup> These experiments have suggested a two-site model for the magnetic structure, in which some Mn sites carry no moment, and others carry a moment of 1–2  $\mu_B$ .

Because the quasicrystal has no translational periodicity, standard *ab-initio* methods could not be applied, and a tight-binding calculation was performed for a cluster of 1500 atoms. This cluster was obtained via a six-dimensional projection algorithm,<sup>15</sup> using a 54-atom "Mackay icosahedron" (MI) as a basic building block. In the cluster, slightly over half of the Mn sites are in the Mackay icosahedra; the remainder reside on "glue" sites that are in regions between the MI. The DOS was calculated only for a central region of roughly 300 atoms; this guaranteed that the effects of the cluster surface were not too large. The parameters and scaling laws for the tight-binding calculation were obtained by fitting to *ab-initio* results for several Al–Mn compounds, some of which were hypothetical.

The total DOS shows no remarkable features; the *d*-resonance has a fairly smooth shape, with no quasigap. However, large fluctuations are seen in the individual Mn-site projected DOS distributions shown in Fig. 6, where Mn(3) is a MI site, and Mn(8) is a glue site. The MI site has a quasigap, while the glue site has a peak at the Fermi level. From the DOS distributions, magnetic moments were calculated using an on-site exchange interaction fitted to *ab-initio* magnetic-moment calculations. These calculations revealed that all of the glue sites are magnetic, while none of the MI sites are. The moments on the glue sites are on the order of 1–2  $\mu_B$ . The total root-mean-square average magnetic moment is consistent with the values inferred from experimental measurements. Thus the calculations support the two-site model of the magnetic structure of this system.

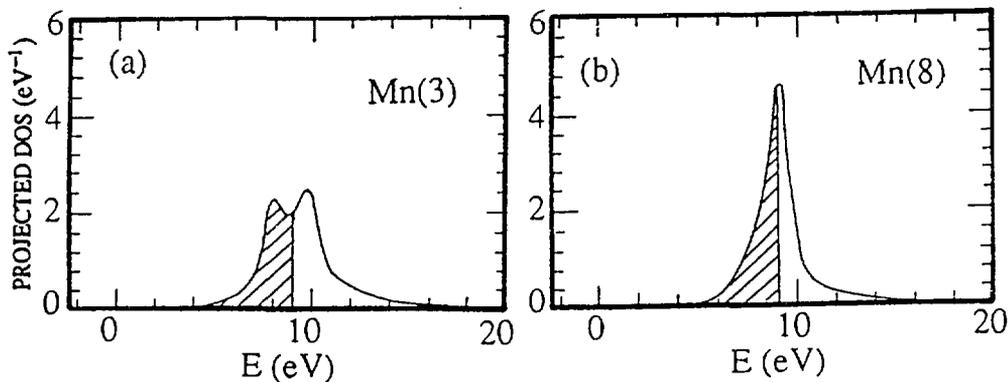


Figure 6. Projected DOS distributions for representative Mn sites in Al-Mn quasicrystal, taken from Ref. 13.

## 6. Conclusions

The above calculations have pointed to the importance of the detailed structure of the transition-metal d-band in determining both the structural and magnetic properties of transition-metal aluminides. At this point, the results are essentially all numerical. It is hoped that future work will obtain a simple physical picture of the origin of the features that were seen above.

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