PAPERS DURING DOE FUNDING PERIOD
(Pre/Reprints Enclosed)

1. "Constant Volume" Pair Potential for Al-Transition Metal Compounds
J. Zou and A. E. Carlsson
Phys. Rev. B (submitted)
2. Phase Stability and Electronic Structure of Transition-Metal Aluminides
A. E. Carlsson
Proceedings of International Conference on the Physics of Transition Metals,
Darmstadt, 1992 (in press) *July 1992*
3. Reply to "Comment on 'Relative Stability of the Al₁₂W Structure
in Al-Transition-Metal Compounds'"
A. E. Carlsson
Phys. Rev. B **45**, 7511 (1992)
4. The Icosahedral Plane-Wave Model: Band-Gap Creation and Band-Tail States
A. E. Carlsson
J. Non-Cryst. Solids (in press)
5. Band Gap Creation by Icosahedral Symmetry in Nearly-Free-Electron Materials
A. E. Carlsson
Phys. Rev. B (submitted)
6. Electronic Structure of Quasicrystalline Al-Mn
H. Deng and A. E. Carlsson
Phys. Rev. Letters (submitted)
7. And Now Quasiseiconductors?"
A. E. Carlsson
Nature **353**, 15 (1991)
8. Band Structures of Non-Magnetic Transition-metal Oxides: PdO and PtO
K. C. Hass and A. E. Carlsson
Phys. Rev. B (Brief Report) (in press)
9. Lattice Imperfections by Lattice Green's Functions
R. Thomson, S. J. Zhou, A. E. Carlsson, and V. K. Tewary
Phys. Rev. B (submitted)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

da
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PHASE STABILITY AND ELECTRONIC STRUCTURE OF TRANSITION-METAL ALUMINIDES

A. E. CARLSSON*

Institut für Festkörperforschung

Forschungszentrum Jülich

D-5170 Jülich, Federal Republic of Germany

**Permanent address: Department of Physics, Washington University,
St. Louis, Missouri 63130, USA*

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

FG 02-84 ER 45130

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 legitimate²) to compare two bands having the same mean-square width μ_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 Al_3Nb , taken from Ref. 4.

3. Simple Intermetallics

Here, we consider the competition between the L_{12} and DO_{22} structures in Al_3T compounds. These structures are both based on an underlying fcc structure, on which the transition-metal atoms form different ordered patterns.³ The L_{12} , or Cu_3Au , structure, has the transition metals in a simple cubic arrangement. In the DO_{22} or Al_3Ti 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 L_{12} structure has the greatest chance of having desirable mechanical properties.

Ab-initio electronic structural-stability calculations have been performed,^{4,5} for these structures using both the augmented-spherical-wave^{6,7} (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 L_{12} structures for the Group III, IV, and V transition metals. All of the results shown here are consistent with experiment;³ Al_3Sc and Al_3Y both form the L_{12} 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 Al_3T compounds, taken from Ref. 4. Open circles indicate results for ideal c/a ratio in 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 Al_3Nb 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 obtained⁸ 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 DO_{22} structure, in which the second shell of transition-metal neighbors is closer than in the L1_2 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^{9,10} were motivated by experimental observations¹¹ that such additions can stabilize the L1_2 structure. The effect of Fe impurities in Al_3Ti , 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 L1_2 structure at around 5% Fe. This is consistent with the observed ternary phase diagram, which has a two-phase field containing the L1_2 and DO_{22} structures centered at roughly 5% Fe. Parallel calculations were performed for Al_3Nb , which indicated that much greater (and impractical) impurity concentrations would be required to stabilize the L1_2 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,³ 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 compared¹² 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) Al_{12}Mn and (b) Al_3Mn , 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 calculations¹³ 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.¹⁴ 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,¹⁵ 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.

Acknowledgements

The author is grateful to the Alexander von Humboldt-Stiftung and to the Forschungszentrum Jülich, where this paper was prepared. M. Methfessel and J. Kübler graciously allowed me to use their relativistic corrections to the ASW code. This work was partly supported by the Department of Energy under Grant number DE-FG02-84ER45130.

References

1. A. E. Carlsson, *Phys. Rev.* **B40**, 912 (1989).
2. D. G. Pettifor and R. Podloucky, *Phys. Rev. Lett.* **53**, 1080 (1984).
3. See P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (ASM, Metals Park, Ohio, 1986).
4. A. E. Carlsson and P. M. Meschter, *J. Mater. Res.* **4**, 1060 (1989).
5. J.-H. Xu and A. J. Freeman, *Phys. Rev.* **B40**, 11927 (1989).
6. A. R. Williams, J. Kübler, and C. D. Gelatt, *Phys. Rev.* **B19**, 6094 (1979).
7. M. Methfessel and J. R. Kübler, *J. Phys.* **F12**, 141, (1982).
8. J. Zou and A. E. Carlsson (unpublished).
9. A. E. Carlsson and P. J. Meschter, *J. Mater. Res.* **5**, 2813 (1990).
10. T. Hong and A. J. Freeman, *J. Mater. Res.* **6**, 330 (1991).
11. The experimental references are given in Ref. 9.
12. A. E. Carlsson, *Phys. Rev.* **B43**, 12176 (1991).
13. H. Deng and A. E. Carlsson (unpublished).
14. See E. Eibschutz, M. E. Line, H. S. Chen, and J. V. Waschczak, *Phys. Rev. Lett.* **59**, 2443 (1987), and references therein.
15. M. Duneau and C. Ogney, *J. Phys. (France)* **50**, 135 (1989).

END

**DATE
FILMED**

2/12/93