Preferred Mn Spacings in Al-Mn Compounds

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A model pair potential is calculated for Mn-Mn pairs in Al using a Green's function method. The pair potential has a preferred spacing of 4.7 Å. The energy resulting from these Mn-Mn interactions strongly favors the Al_6Mn, α-AlMnSi, and icosahedral quasicrystal structures relative to competing simple structures, providing a possible mechanism for stabilizing the complex structures.

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Al-rich compounds with Mn form a bewildering variety of complex structures, including crystalline structures with large unit cells [1], as well as metastable quasicrystalline structures [2]. However, the origins of this structural complexity has not yet been definitely established. *Ab initio* band-structure calculations [3,4] have pointed to the importance of quasigap effects, in which a reduction of the electronic density of states (DOS) around the Fermi level is believed to stabilize in the complex phases. Unfortunately, these calculations do not provide an intuitive picture of the underlying physics, in the sense of supplying simple criteria for stability or metastability of a given structure. A modified form of nearly-free-electron perturbation theory [5–7] has indicated the importance of characteristic electron counts and filling of "Jones zones" in k space. The treatment of transition metals in such calculations is still incomplete, despite significant progress [5]. A real-space analysis based on the effective-medium theory (EMT) [8] indicated a preference for certain local packing motifs, in particular Mn surrounded icosahedrally by Al. However, the connection between these background-density constraints of the EMT and the quasigap effects has not been made clear. In addition, the structural-energy differences obtained by the EMT are sometimes much smaller than those obtained by *ab initio* methods [4]. In this Letter, we calculate a Mn-Mn interaction potential which demonstrates a new effect: the existence of a characteristic preferred spacing of 4.7 Å between Mn atoms. We show that the pair potential provides a major ingredient in the stability of these structures, even though they have no nearest-neighbor Mn-Mn contacts. In addition, we show that a large number of Mn-Mn pairs at the preferred spacing leads to quasigap effects in the electronic DOS. Thus our description contains a large part of the physics of the *ab initio* and nearly-free-electron calculations.

The methodology of the pair potentials is outlined in a previous paper [9,10]. They are obtained from the total energy of two d-like impurities in a uniform electron gas. The electronic wave functions are built out of electronic plane-wave states $|\mathbf{k}\rangle$, and localized d orbitals $|d,m,a\rangle$ and $|d,m,b\rangle$, where a and b denote the Mn atoms containing the d shells. The Hamiltonian is

$$H=\sum_{\mathbf{k}} \epsilon_k |\mathbf{k}\rangle\langle\mathbf{k}| + \sum_{m=-2}^{2} \epsilon_d |d,m,a\rangle\langle d,m,a| + \sum_{m=-2}^{2} \epsilon_d |d,m,b\rangle\langle d,m,b| + \sum_{\mathbf{k}m} [V_{\mathbf{k}am} |\mathbf{k}\rangle\langle d,m,a| + \mathrm{H.c.}] + \sum_{\mathbf{k}m} [V_{\mathbf{k}bm} |\mathbf{k}\rangle\langle d,m,b| + \mathrm{H.c.}]\,, \qquad (1)$$

with a simple parametrized form for the $\mathbf{k}-d$ couplings

$$V_{\mathbf{k}am} = V_0 (k/k_0)^2 \exp(-k/k_0) Y_{2m}(\theta_{\mathbf{k}}, \phi_{\mathbf{k}})$$

and

$$V_{\mathbf{k}bm} = \exp(-i\mathbf{k}\cdot\mathbf{R}_{ab}) V_{\mathbf{k}am}\,.$$

The parameters in $V_{\mathbf{k}d}$ are obtained via fits to *ab initio* calculations for single impurities, by insisting that the first three moments of the DOS match [11]. The electronic DOS is obtained via a Green's function technique. Thus only indirect interactions between the Mn atoms, mediated by the electron gas, are included. These potentials are therefore appropriate for structures in which there are no Mn-Mn nearest-neighbor contacts.

The resulting Mn-Mn pair potential is shown in Fig. 1. It depends parametrically on the background electron density, which is chosen to be 0.18 $Å^{-3}$, typical for Al-Mn intermetallics near the quasicrystal composition. For comparison, we show a Ti-Ti potential obtained in the same fashion, and an Al-Al potential [12] obtained by the usual second-order perturbation theory. The latter has the well-known asymptotic form

$$V_2^{\mathrm{eff}} \propto \left[\frac{|V_{\mathrm{ps}}(2k_F)|^2}{E_F}\right] \cos(2k_F r)/r^3\,. \qquad (2)$$

Here V_{ps} is the ionic pseudopotential for Al. The Mn-Mn potential is the strongest in magnitude; the Ti-Ti potential is somewhat weaker, and the Al-Al potential is an order of magnitude weaker. In addition, there are relative phase shifts between the potentials. These effects may be partly understood via the asymptotic large-r behavior of the transition-metal–transition-metal potentials:

$$V_2^{\mathrm{eff}} \propto E_F (2l+1)^2 \cos[2k_F r - \delta(N_d)]/r^3\,. \qquad (3)$$

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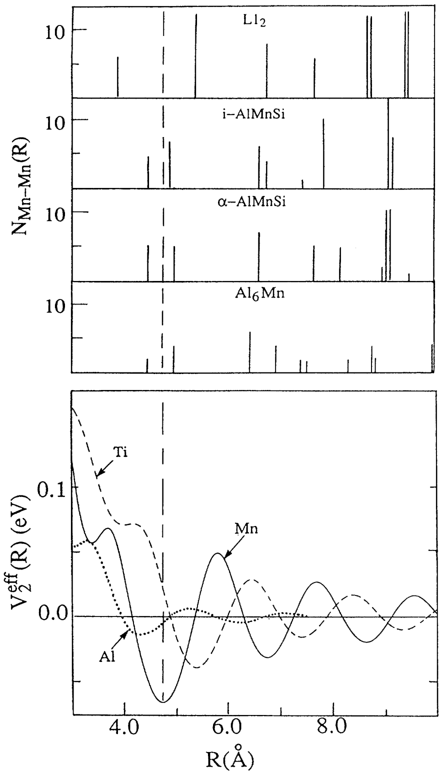

FIG. 1. Effective pair potentials for Mn pairs and Ti pairs in Al and effective pair potentials between Al ions in pure Al. Distribution functions $N_{\text{Mn-Mn}}$ indicate the number of Mn-Mn pairs vs separation in Al-Mn intermetallic compounds. Vertical dashed line is placed at the minimum of Mn-Mn potential.

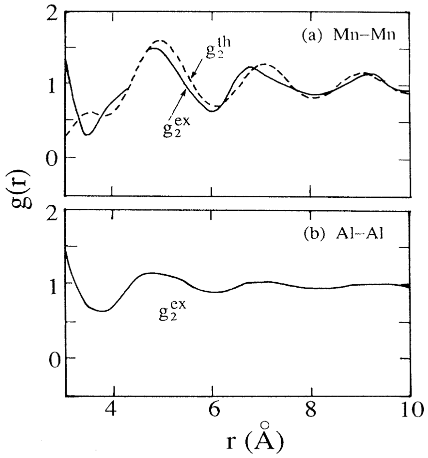

FIG. 2. Pair distribution functions in liquid $Al_{80}Mn_{20}$.

The strength of the transition-metal potentials relative to that for Al can thus be explained by a combination of the weakness of the Al pseudopotential at $2k_F$ relative to E_F, and the l-dependent prefactor in the transition-metal potential, which shows that the strength of the potential increases as one goes from s- and p-wave scattering to d-wave scattering. The phase shifts are connected with the quantity $\delta(N_d)$ in the transition-metal potential, which varies systematically from 2π to 0 as the transition-metal d band fills. Although this asymptotic form is not valid in the 5 Å region of interest here, the relative strength of the Mn-Mn potential in this region is certainly enhanced by the strong scattering due to Mn, and also the orbital multiplicity. In addition, the minima of the potential display a characteristic band-filling dependence similar to that of Eq. (3).

We expect this mediated Mn-Mn potential to be the dominant interaction at the second-neighbor spacing and beyond. As seen above, it is much stronger than the Al-Al potential; since the Al-Mn potential contains one power of the weak pseudopotential V_{ps}, we also expect the Al-Mn interaction to be weaker than the Mn-Mn interaction. These expectations are confirmed by two calibration tests that we have performed for the potentials. The first involves the partial structure factor $g^{\text{expt}}_{\text{Mn-Mn}}(r)$ for Mn-Mn pairs in liquid $Al_{80}Mn_{20}$ (with an electron density of 0.16 Å^{-3}). The experimental results of Maret *et al.* [13] are compared in Fig. 2 to the quantity

$$g^{\text{theor}}_{\text{Mn-Mn}}(r)=\exp[-V_2^{\text{eff}}(r)/k_BT]\,. \qquad (4)$$

This form for $g_{\text{Mn-Mn}}(r)$ is not exact, but analysis based on both the Born-Green theory [14] and a low-density expansion [15] for the Mn solutes suggest a form of the type given here, perhaps multiplied by a prefactor of order unity. As seen in Fig. 2, the agreement of the experimental and theoretical results is excellent, with the maxima of the liquid pair-correlation function coinciding very closely with the minima of V_2^{eff}. We note also that the oscillations in the Mn pair-correlation function at distances of more than 4 Å are much stronger than those of the Al pair-correlation function. This is consistent with our finding that the Mn-Mn potential is stronger than the Al-Al potential.

The other calibration test involves structural-energy differences for hypothetical fcc-based DO_{22} and $L1_2$ structures (with the ideal c/a ratio for the DO_{22} structure). In both of these structures, each transition-metal atom has twelve nearest Al neighbors (in an fcc arrangement); each Al atom has four transition-metal neighbors and eight Al neighbors. Despite these short-range similarities, the *ab initio* structural energy difference [16] is large, 0.42 eV/Mn atom favoring the DO_{22} structure. This large value by itself suggests that medium- or long-range interactions may be important. In comparison, our model gives 0.30 eV/Mn atom. Given the simple nature of our model, this agreement is remarkably good. We have also shown [9] that the chemical trends in the $L1_2$-DO_{22} energy for the $4d$ aluminides are well described by this type of potential. Our preliminary studies [17] of the effects of the Al-Al and Al-Mn interactions, using a pseudopotential expansion, indicate that the Mn-Mn potential gives the dominant contribution to this structural-energy difference.

We now show that these interactions correctly describe the stability of several observed and hypothetical Al-Mn and Al-Ti compounds, at compositions near that of the quasicrystal. There are no nearest-neighbor Mn pairs in these compounds, so our mediated pair potential is applicable. The results are shown in Fig. 3. The coordinates of the crystalline structures are obtained from standard tabulations [1]. The coordinates of the icosahedral quasicrystal are obtained from the procedure of Duneau and Oguey [18], involving a six-dimensional projection algorithm. To our knowledge, this is the most accurate existing model for icosahedral Al-Mn. The quantity plotted is $E_2^{\mathrm{Mn\text{-}Mn}}$, which is simply the total energy per Mn atom resulting from the calculated Mn-Mn pair potential [19]. Of the structures that are treated, only the Al_6Mn, α-AlMnSi, and icosahedral quasicrystal structures actually form. The α phase is believed to be closely related to the quasicrystal; the Al_6Mn structure is less closely related but is complex in the sense that it has fourteen atoms per primitive unit cell. These are precisely those which have the lowest values of $E_2^{\mathrm{Mn\text{-}Mn}}$, suggesting that the Mn-Mn interactions are important in stabilizing the complex structures. We note that the structural energy stabilizing these complex structures relative to the hypothetical $L1_2$ structure is large, roughly 0.5 eV. This is consistent with the energy scales obtained by *ab initio* calculations for other aluminides [4,20,21], and significantly exceeds the values obtained by the EMT [8]. In addition, the quasicrystal is only slightly above the Al_6Mn and α-AlMnSi structures, and lower in energy than all of the other crystalline structures. This suggests that it could be metastable; an accurate determination of the metastability would necessitate the inclusion of a variety of short-range interactions which are not included in the present analysis. In contrast, for Ti the complex structures have higher energies than the observed fcc-based ones, consistent with the observed transition from "simple" to complex structures with increasing d-electron count.

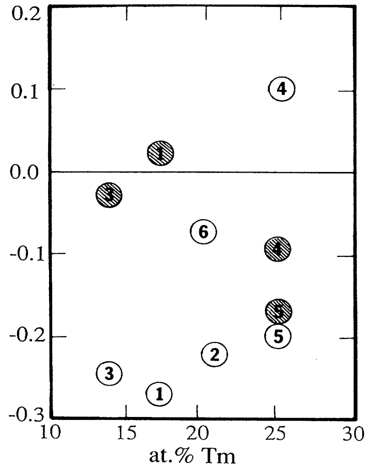

FIG. 3. Contribution E_2^{LR} of Mn-Mn interactions to structural energies in several Al-Mn and Al-Ti intermetallics; shaded circles are Al-Ti. Legend for structures is as follows: (1) α-AlMnSi; (2) icosahedral quasicrystal (from Ref. [16]); (3) Al_6Mn structure; (4) $L1_2$ structure; (5) DO_{22} structure, and (6) Ni_4Mo structure.

These results can be understood via the histograms for Mn-Mn spacings shown in Fig. 1. The Mn pair potential has a pronounced minimum at around 4.7 Å. In the α phase, icosahedral quasicrystal, and the Al_6Mn structure histogram, a large number of Mn-Mn pairs are found near this distance. In each case, the pairs at around 4.7 Å contribute roughly -0.3 eV to $E_2^{\mathrm{Mn\text{-}Mn}}$, and thus dominate its large negative values. The contrasting plot for the $L1_2$ structure shows relatively unfavorable Mn-Mn spacings. The importance of the preferred 4.7 Å, spacing of Mn atoms is supported by the different DOS plotted in Fig. 4. The quantity plotted is the change in the DOS induced by taking a pair of Mn atoms at infinite separation, and bringing them to the preferred separation. This results in a reduction in the DOS around the Fermi level for Mn. The magnitude of the reduction is such that if one summed up over ten neighbors (as in the α phase) at this distance, the total DOS would be reduced relative to its single-impurity value by roughly 40%. Thus, the pairs at the preferred separation lead to a pronounced quasigap in the electronic DOS, which, as indicated above, stabilizes the complex structures in *ab initio* calculations. It appears then that V_2^{eff}, and in particular the well around 4.7 Å, capture the dominant physics of the *ab initio* calculations. The contrasting Ti results do not have such a pronounced DOS reduction. This suggests that Mn and other transition metals with nearly half-filled d bands may be special with regard to quasigap formation in the complex structures.

We now show that these tendencies penalize the formation of simple fcc- or bcc-based intermetallic compounds,

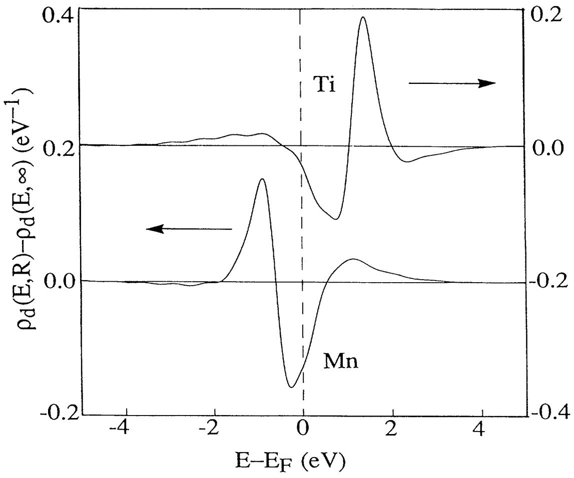

FIG. 4. Different density-of-states distributions for interacting Mn pairs and Ti pairs in Al.

and thus lead to the formation of complex structures. Inspection of Fig. 1 suggests three simplified criteria that should be fulfilled for energetically stable phases. First, there should be a large number of spacings around the 4.7 Å value. Second, no spacings of less than approximately 4.3 Å should be present. Finally, there should be no Mn-Mn pairs inside the first peak, between 5.4 Å and 6.3 Å. If one attempts to place neighbors around the optimal value in an fcc-based structure with the appropriate density (which corresponds to a lattice constant of 3.8 Å), one finds that the Mn-Mn pairs must sit at the third-neighbor distance, with separations in $(1,\frac{1}{2},\frac{1}{2})$-type directions. However, as one fills neighbor shells in this fashion, one rapidly finds that the Mn atoms begin to impinge on each other. In fact, without having Mn-Mn separations of less than 4.3 Å, or inside the first peak, one can surround a central Mn with at most six other Mn at the preferable distance. In comparison, each Mn atom in the α phase has ten such neighbors. On the other hand, if one goes to bcc-based structures (now with a lattice constant of 3.0 Å), the best possibility is to place the Mn-Mn neighbors at $(\frac{3}{2},\frac{1}{2},\frac{1}{2})$-type positions. This corresponds to a spacing of 5.0 Å. Again, one can have only six such neighbors without causing short Mn-Mn spacings. Thus complex structures form instead of fcc- or bcc-based simple structures.

In conclusion, we have seen that the existence of a preferred Mn-Mn spacing of 4.7 Å is a major factor in the stability and metastability of complex Al-Mn compounds. Further work should amplify this conclusion by performing atomistic simulations using a potential-energy function which, in addition to the Mn-Mn interactions, includes other shorter-range Al-Al and Al-Mn interactions. Work on developing such a methodology is currently under way [17].

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