

Symmetry-induced local magnetic moments in icosahedral Al-Mn alloys

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Electronic-structure calculations of icosahedral Al-Mn clusters suggest well-defined quasiatomic Mn moments. The driving force for moment formation is a large Mn d density of states at the Fermi energy in a non-spin-polarized calculation. The onset of Mn magnetism results directly from the local coordination in the icosahedral environment, which does not split the Mn $3d$ levels and inhibits Al-Mn $sp-d$ hybridization.

The experiments of Shechtman *et al.*¹ demonstrating icosahedral symmetry in rapidly solidified $\text{Al}_{0.86}\text{Mn}_{0.14}$ have produced a torrent of studies aimed at elucidating the structure and properties of quasiperiodic materials. Many theoretical approaches to characterizing structure-property relationships in quasicrystals have been based on the Penrose lattice,^{2,3} a nonperiodic tiling of the two-dimensional plane, and the one-dimensional analogue, the Fibonacci lattice.⁴ The methods employed have been by necessity schematic, e.g., tight-binding Hamiltonians for noninteracting electrons,⁵ the philosophy being to identify topologically induced features in the electronic structure which are expected to persist qualitatively (even in higher spatial dimensions) when more realistic computational techniques are used. One of the most striking features which has emerged from the electronic structure of a two-dimensional Penrose lattice² is the occurrence in the density of states of a peak of zero width associated with localized states which appear to be induced only by local lattice structure (i.e., not by the quasiperiodicity of the lattice).

While a comprehensive characterization of the electronic structure of a three-dimensional quasicrystal comparable to state-of-the-art band-structure calculations is not yet feasible, inroads can nevertheless be made by considering features in the electronic structure resulting directly from local icosahedral symmetry. A prior calculation by McHenry *et al.*⁶ compared the electronic structure of Al and Al-Mn clusters chosen to represent local environments of fcc (cubo-octahedral, O_h symmetry) and quasicrystalline (icosahedral, I_h symmetry) phases, respectively. The authors inferred that the I_h Al clusters were more stable than their O_h counterparts and found that Mn atoms placed at the center of the I_h cluster produced a sharp predominantly Mn d peak in the density of states near the Fermi energy E_F . The large density at E_F pointed to the inherent instability of this configuration, though it has been noted that moment formation could enhance the stability of such a configuration.⁷

This Brief Report goes beyond earlier results of McHenry *et al.*⁶ in three respects. First, additional calculations are done in the spin-unrestricted mode so that local Mn moments can be evaluated. Second, we focus

on the consequences of I_h symmetry for magnetism and use our results to interpret recent experimental data. Finally, we find important new aspects of chemical bonding in icosahedral Al-Mn that address the role of chemistry in icosahedral stability, a feature lacking in other recent calculations.²⁻⁵

This work is motivated in part by recent magnetic measurements in quasicrystals which reveal the existence of a large local moment on the manganese site⁸⁻¹⁰ as well as spin-glass behavior at low temperature,⁸ neither of which is evident in the corresponding crystalline phases of Al-Mn. Further, heat capacity, electron transport, and optical properties have been reported to be strongly influenced by scattering by resonant Mn d states in the conduction band, which have been interpreted as arising from the existence of Mn virtual bound states at the Fermi level in the quasicrystals.^{11,12} These results and earlier heat-capacity results⁹ suggest that only a small fraction of the manganese atoms contribute to magnetism and to d -resonance states in these materials. This behavior suggests that in quasicrystals, even with Mn concentrations of 14–22 at. %, a certain fraction of the Mn sites behaves like dilute impurities in an Al host.

In this Brief Report one possible explanation of this behavior is discussed. In lower-symmetry sites Mn atoms are shown to effectively form directional $p-d$ hybrid bonds which removed Mn d character from the Fermi level, thus reducing the moment-forming capabilities of the Mn sites, an idea consistent with expectations based on crystal-field effects alone. In Mn-centered icosahedral Al the absence of crystal-field effects inhibits the breakdown of intra-atomic correlations (i.e., the d orbitals transform according to the fully fivefold degenerate H_g irreducible representation of the I_h group). Further, markedly diminished $sp-d$ matrix elements result from the orientational incommensurability between the $3d$ orbitals and the fivefold rotational axes of the icosahedron. It is possible that the above-mentioned anomalies in magnetic and resistive properties may also be adequately explained by clustering of Mn atoms in the quasicrystals. However, the influence of symmetry upon the moment formation of Mn in aluminum provides an interesting and provocative perspective on a classic problem in solid-

state physics.

Our calculations were carried out with the multiple-scattering $X\alpha$ (MS $X\alpha$) cluster technique to examine the electronic structure of an Al_{18}Mn cluster representing a Mn impurity coordinated by first- and second-nearest-neighbor Al atoms in O_h symmetry, Al_{32}Mn , which represents Mn surrounded by two coordination spheres in icosahedral symmetry, and MnAl_9 , which represents Mn in a low-symmetry (D_{3h}) environment, possibly representative of an intericosahedral region. Figures 1(a) and 1(b) show the MS- $X\alpha$ energy levels for the non-spin-polarized O_h Al_{18}Mn cluster as compared with those of the I_h Al_{32}Mn cluster. We note first that the ground-state configuration of the Al_{18}Mn is nonmagnetic. A cluster moment of $1 \mu_B$ is observed, but this can be explained simply as the result of the fact that Mn has an odd number of electrons and successive Al shells always have an even number of electrons in O_h symmetry. Thus the cluster moment may be an artifact of an unpaired electron on the manganese site, which disappears if one allows fractional occupation. Recent spin-polarized calculations on an O_h MnAl_{18} cluster using a Gaussian orbital basis set¹³ also revealed a cluster moment of $1\mu_B$ but with a $1.5\mu_B$ local moment on Mn which was partially compensated by an antiferromagnetic coupling to the Al conduction band. This small local moment is inconsistent with experimental observations of nonmagnetic Mn impurities in fcc Al and may well also be an artifact of the odd number of electrons in a finite cluster as was noted in Ref. 13. For systems near the magnetic instability as is Mn in fcc Al (it is observed to be a spin-fluctuation system),¹⁴ the exclusion of host band-structure

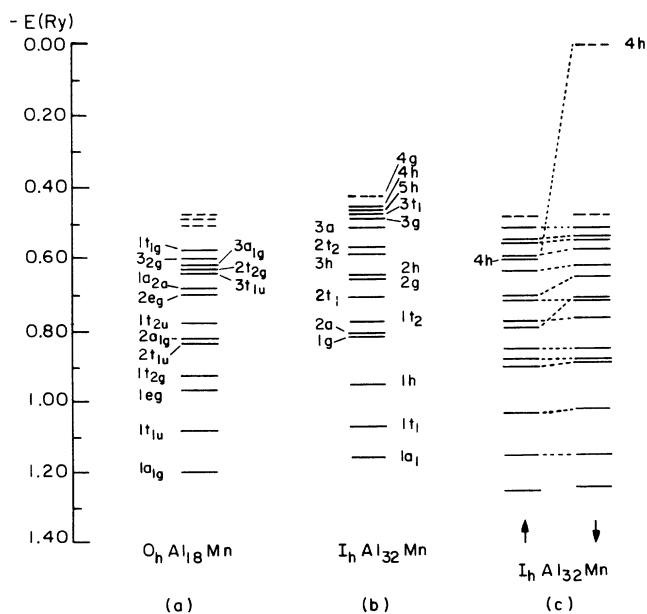


FIG. 1. The MS $X\alpha$ energy levels for (a) MnAl_{32} , (b) MnAl_{18} , and (c) MnAl_9 (spin-polarized) labeled according to the irreducible representations of the I_h [(a) and (c)] on O_h [(b)] point groups. Occupied and unoccupied orbitals are indicated by solid and dashed lines, respectively.

effects in the cluster representation due to the small spatial extent of the cluster may well prove to be a less than adequate representation in these systems. However, features in the bonding do help to explain the lack of a strong local moment in Mn as well as the small or non-existent exchange splitting in these systems. The energy levels for the D_{3h} cluster (not shown) are characterized by eigenfunctions showing strong d - sp (Mn-Al) mixing throughout the manifold. This cluster could not be made to sustain a moment.

In the O_h Al_{18}Mn cluster the hybridization between Al-Mn states is observed predominantly in the upper bands. The low-lying states are of Al s -Mn d bonding character, whereas the $3e_g$ and $2t_{2g}$ levels just below the Fermi level are Al p -Mn d bonding in character. The octahedral crystal field of the neighboring Al atoms is such that the Mn d states are split into threefold degenerate t_{2g} states and twofold degenerate e_g states (sixfold and fourfold degenerate counting spin degeneracy). These representations are uniquely qualified for directed nearest-neighbor σ bond formation between Al p and Mn d states in the case of the $2t_{2g}$ level and between Mn d and second nearest neighbor Al p states for the $3e_g$ level as illustrated in Fig. 2. The effect of this bonding on moment formation is twofold: (1) The p - d hybrid bonding results in lower-energy states, which effectively removes

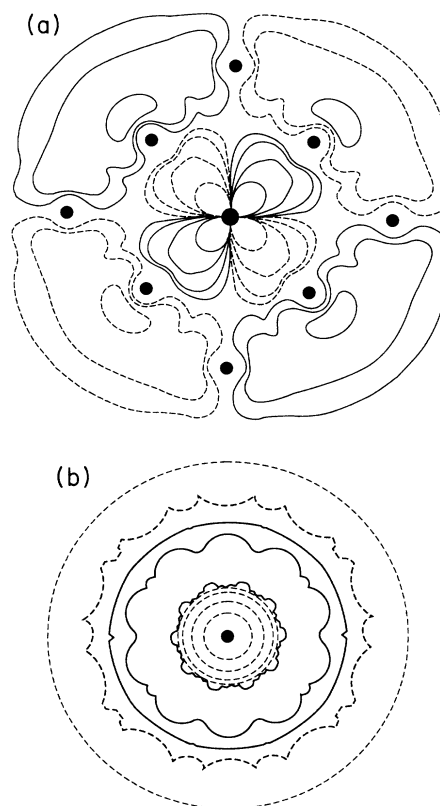


FIG. 2. The (a) $2t_{2g}$ orbitals of Al_{18}Mn plotted in the xy plane and (b) the $4H_g$ orbital of Al_{32}Mn plotted in the xy plane. Positive and negative values of the wave function are indicated by solid and dashed lines, respectively, and the contour values are ± 0.081 , ± 0.027 , ± 0.009 , and ± 0.003 .

Mn d states from the Fermi level; (2) the t_{2g} - e_g splitting results from the disparity in bonding between the Mn with first and second nearest neighbors, respectively and thus acts to broaden the manifold associated with Mn d character as compared with a more atomiclike configuration. Because of these bonding states the total Mn-Al manifold is slightly more stable for the O_h cluster than for the I_h cluster.

In Fig. 1 are shown the MS $X\alpha$ energy levels for the $Al_{32}Mn$ cluster in I_h symmetry as well as for the spin-polarized counterpart. Two pertinent features of the non-spin-polarized states should be emphasized. First a contraction of and movement to slightly lower energies of the Al manifold in the I_h clusters leaves atomiclike Mn d states at the Fermi level. Second this Mn d manifold is degenerate in the I_h crystal field and forms no significant bonding with the aluminum p orbitals as shown in Fig. 2. This configuration thus yields a sharply peaked narrow Mn d band at E_F (Fig. 1) which is an ideal situation for local moment formation. As shown in Fig. 1(c) this H_g state drives the $Al_{32}Mn$ complex to develop a sizable local moment of $3.6\mu_B$ on the Mn site, which is partly compensated by an antiferromagnetic coupling with the Al conduction electrons, so that a total cluster moment of $3.0\mu_B$ is observed. The overall exchange splitting induced on the Al subband is small but the exchange splitting associated with the Mn d states is as much as ~ 8 eV, and is therefore nearly atomiclike.

Although Mn shows well-defined magnetic behavior in both an I_h aluminum environment and an O_h copper environment with calculated magnetic moments of $3.5\mu_B$ (Ref. 15) and $3.6\mu_B$, respectively, there are two notable differences: (1) The Mn exchange splitting is considerably larger for I_h $Al_{32}Mn$ (~ 8 eV) than for O_h $Cu_{18}Mn$ (~ 2 eV); (2) the $3d$ charge density as shown in Fig. 2 for the highest occupied H_g orbital in I_h $Al_{32}Mn$ is considerably more localized around Mn than the corresponding T_{2g} and E_g orbitals in $Cu_{18}Mn$.¹⁵

Whether one adopts the Friedel-Anderson virtual bound-state model^{16,17} or the Schrieffer-Hirst^{18,19} configuration-based approach, the electronic structure of dilute $3d$ impurities in metallic hosts results from the competition between intra-atomic correlations of the impurity and from covalent ($sp-d$) mixing between the $3d$ electrons and the conduction electrons of the host. This delicate balance between competing interactions is illustrated by the contrasting electronic structures of the $3d$ transition metals when dissolved in copper or in aluminum. The

well-defined moments associated with several transition metals in a copper environment have been adequately reproduced in earlier calculations.¹⁵ The magnetism of these impurities in crystalline Al is nearly completely absent, while local moments are stable in our calculations for Al-Mn in I_h symmetry. The stability of the magnetic moment in either the Cu and I_h aluminum environments arises from the dominance of the Mn intra-atomic correlation energy over the impurity-host bonding energy. As discussed earlier the icosahedral environment promotes magnetism of Mn in Al by inhibiting both the breakdown of intra-atomic correlations and the formation of impurity-host bonding. The effect is clearly promoted by symmetry rather than chemistry, as the associated cubooctahedral complex exhibits much weaker magnetism. The precursor to magnetism in the icosahedral case can be understood by the character of the non-spin-polarized density of states, which reveals a high density of Mn d character at E_F .⁶ The Mn character in O_h Al is below E_F by virtue of its bonding character and is broader due to the t_{2g} - e_g splitting.

We conclude by saying that the contrast in the electronic states of Mn in I_h and O_h environments provides a new perspective to the problem of characterizing local magnetic moments in metals by highlighting the role of local symmetry as a barrier or aid to $sp-d$ mixing. We believe this offers a plausible explanation for observed local moments and the impuritylike scattering for certain Mn sites in quasicrystalline Al-Mn. Admittedly this is not the only explanation. It has been suggested that the increased Mn moment could be due to Mn-Mn clustering. Such clustering is manifest in Mn-Al phases (β -Al-Mn-Si) but with only modest increases in the moment.²⁰ Further, the moment in quasicrystalline Mn-Al is significantly larger than in its crystalline counterparts. As only a fraction of the Mn atoms present in Al-Mn quasicrystals is required to account for the observed moment formation, it can be inferred, from the calculation on the low-symmetry D_{3h} cluster, that the remaining Mn atoms occupy low-symmetry, not moment-forming sites, where through bond formation the bond strain inherent to the nonperiodic structure is relieved.

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