

Magnetism of Al-Mn quasicrystals

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The effect of symmetry and concentration of Mn on the magnetism of Al-Mn quasicrystals has been investigated through self-consistent density-functional calculations using molecular clusters and supercell band-structure schemes. A single Mn atom surrounded by 54 Al atoms in an icosahedral or a cuboctahedral structure is found to be nonmagnetic. However, as the Mn concentration is increased, moments develop on Mn sites whose magnitude and coupling depend on their location.

It is increasingly becoming apparent that size, symmetry, dimension, and local environment play an important role in the magnetism of transition-metal atoms.¹ It has been shown that an otherwise nonmagnetic system can become magnetic when its dimension is reduced² and symmetry is enhanced.³ The former is governed by the increasing localization of electron orbitals whereas in the latter it is the degeneracy of the orbitals driven by high symmetry that governs the magnetic behavior.

Quasicrystalline materials⁴ offer a system where both the effect of symmetry and size are intertwined. Consequently, the magnetism of these systems provide a fertile ground where the competition between the two can be studied. In this regard there has been a rich variety of experiments⁵ available on Al-Mn systems forming ordered octahedral arrays, quasicrystalline systems as well as amorphous alloys. It has been shown⁵ that Mn in the ordered structure (Al₈₆Mn₁₄) is nonmagnetic whereas in the quasicrystalline system, containing the same manganese concentration, there is a distribution of Mn sites with differing moments. The Al-Mn quasicrystalline alloys with Mn concentration less than 5% are, however, nonmagnetic.⁶

The comparison of the ordered and quasicrystalline Al-Mn would indicate that the symmetry plays a role on magnetism. On the contrary, the comparison of the quasicrystalline Al-Mn at increasing Mn concentration⁵ would indicate that it is not only the symmetry but also the Mn-Mn interaction that plays a decisive role. This is further borne out by the experiments involving amorphous systems.

There have been three theoretical attempts to our knowledge to explain the above magnetic behavior. Two of these calculations used clusters as models and were carried out within the density-functional formalism. The studies by McHenry *et al.*⁷ used 33 atom clusters having

fcc and icosahedric symmetry. Using the MS-X α scheme they showed that the Al₃₂Mn cluster in the icosahedric form develops a moment of $3.6\mu_B$, while that in a fcc structure is nonmagnetic. Bagayoko *et al.*⁸ also carried out calculations on Al₁₈Mn fcc structure and their results for this system were in qualitative agreement with that of McHenry *et al.* Using their cluster results McHenry *et al.* predict that the Mn sites in quasicrystallines (QC's) are magnetic because of symmetry. This result is at odds with the experiment,⁶ since the Al-Mn alloy are nonmagnetic when Mn concentration is less than 5%. As a matter of fact, a band-structure calculation by Fujiwara⁹ on the same system yielded a small density of states at the Fermi energy implying a nonmagnetic ground state. The question then remains: Is the magnetism observed by McHenry *et al.*⁷ in the icosahedric cluster an artifact of the cluster size or is it due to the approximation of the potential inherent in the MS-X α scheme?

In this report we present a systematic study of the Al-Mn system using both clusters (with no approximation to the form of the potential) and supercell band-structure method, which we believe, illustrates how the symmetry and the Mn-Mn interaction jointly affect the magnetism of quasicrystals. The cluster model was used to study the effect of concentration and site location of Mn on its magnetic moment. The supercell band-structure study on a specific Al-Mn system was carried out to ensure the credibility of the cluster results.

Our cluster studies are based on a spin-polarized linear combination of atomic-orbitals molecular-orbital approach (LCAO-MO) and are carried out for cuboctahedric and icosahedric structures. We first study clusters having a central Mn surrounded by Al atoms. For this part of our work, we have studied cuboctahedric clusters containing 12 and 18 Al atoms, and icosahedric clusters having 12, 24, 32, 42, 44, and 54 atoms. The

studies on icosahedric clusters were carried out on two families of icosahedra. Sizes 12, 24, 44, and 54 correspond to a central Mn with Al atoms in a regular icosahedric growth. We have also considered sizes 32 and 44 corresponding to a dodecahedron (DI) of 32 atoms and a further decoration by 12 apex atoms. Our cluster work differs from similar studies by McHenry *et al.*⁷ in that the theoretical scheme employed by us^{10,11} does not make spherical shape approximation inherent in the MS-X α scheme employed by them. In addition, we extend our studies to larger sizes. Contrary to the results of McHenry *et al.*, we show that a single Mn site does not carry any moment in icosahedric or cuboctahedric environment and therefore the icosahedric environment alone is not enough to stabilize the Mn moment. To ensure that this result is not influenced by cluster size, we performed a supercell calculation¹² on MnAl₅₄ cluster to check the effect of finite cluster size. We found that the Mn sites are again nonmagnetic. Since the symmetry alone does not stabilize moment formation, we performed cluster calculations with clusters having more than one Mn atom. These studies show that neighboring Mn sites do develop moments thus suggesting that Mn-Mn interactions may be responsible for the moment formation.

We start by briefly describing the theoretical schemes used by us. For the work involving a single Mn surrounded by Al atoms, the calculations were carried out using a linear combination of atomic-orbitals molecular-orbital (LCAO-MO) approach. The wave functions were expanded in terms of Gaussian basis functions¹⁰ and the exchange-correlation effects were incorporated within the density-functional scheme. To simplify the calculations, norm conserving pseudopotential¹² were used to replace the core effects for Al atoms. The basis sets involved 12s, 7p, and 4d uncontracted Gaussian functions for Mn and 5s, 3p Gaussian functions for Al and were obtained from a nonlinear fit of atomic orbitals obtained via a numerical solution of the atomic Schrodinger equation.¹⁰ Further, the symmetry groups were used to render the calculations tractable. The details of the calculation are described elsewhere and we refer the reader to our earlier paper¹⁰

for details. Even after all the simplifications, calculations involving Gaussian-type orbitals (LCAO-MO-GTO) are computationally heavy and a study of clusters containing several Mn atoms was not possible. To carry out the later portion of our work, we used a computationally less demanding approach called the discrete variational method (DVM).¹¹ Here, the molecular wave function is expressed as a linear combination of atomic orbitals taken in a numerical form on a radial mesh of points. For Al, the basis functions included 2s, 2p, 3s, 3p, and 3d orbitals, while for Mn we included 3s, 3p, 3d, 4s, and 4p orbitals in the basis set. The remaining core orbitals were frozen. The Hamiltonian and overlap integrals required to solve the molecular Rayleigh-Ritz equation were calculated via numerical integration on a mesh of 3000 points around Al and Mn. These points were found to be sufficient for the convergence of the electronic spectrum to within 0.01 eV. All our calculations are based on the spin-polarized version of the density-functional theory. The molecular density of states were obtained by placing Lorentzians of width α at the molecular-orbital energies. For local density of states, each molecular eigenvector was projected to the atomic sites with a weight taken from the Mulliken population analysis of the eigenvector. The magnetic moment was determined by integrating the spin-up and the spin-down density of states up to the Fermi energy.

To investigate any effects arising due to finite sizes in cluster calculations the above studies were repeated using a band-structure model with a supercell of 55 atoms. The supercells which have icosahedric symmetry were then arranged on a bcc lattice. The calculations were based on the linear-muffin-tin-orbitals (LMTO) method using the local-density, scalar-relativistic, and atomic-sphere approximations.¹³ The core states of the constituent atoms (1s-2p for Al and 1s-3p for Mn) were frozen. There are nine valence states per sites consisting of s, p, and d orbitals. With 55 atoms per unit cell, this leads to 495 \times 495 overlap and Hamiltonian matrices. The self-consistency procedure employed eight *K* points in the Brillouin zone, which is equivalent to a point calculation with double the

TABLE I. Local magnetic moment (in μ_B) on a Mn site in MnAl_n clusters.

Geometry	Cluster	Theoretical scheme		
		LCAO-MO-GTO	DVM	Super cell
	Mn atom	5.0		
Regular Icosahedron	MnAl ₁₂	3.31	3.36	
	MnAl ₂₄	1.61		
	MnAl ₄₂	0.08	0.11	
	MnAl ₅₄	0.05	0.01	0.01
Dodecahedron	MnAl ₃₂	2.90		
	MnAl ₄₄	0.09		
Octahedron	MnAl ₁₂	3.66	3.38	
	MnAl ₁₈	2.08		
	MnAl ₄₂		1.04	
	MnAl ₅₄		0.08	

TABLE II. s , p , and d decomposition of the spin-up, spin-down, and the total charge in orbitals transforming according to representations t_{2g} , and e_g for Oh, and H_g for Ih clusters.

Cluster	Spin-up			Spin-down			Total		
	s	p	d	s	p	d	s	p	d
MnAl ₁₂ (Oh)	4.19	1.12	4.69	4.01	0.98	1.03	8.20	2.10	5.72
MnAl ₁₈ (Oh)	6.59	1.40	4.01	6.56	2.52	1.93	13.15	3.33	5.94
MnAl ₁₂ (Ih)	4.40	0.93	4.67	3.89	0.75	1.36	8.29	1.68	6.03
MnAl ₂₄ (Ih)	8.18	7.96	3.86	8.10	4.65	2.25	16.28	12.61	6.11
MnAl ₄₂ (Ih)	7.48	9.56	2.97	7.46	9.65	2.89	14.94	19.21	5.86
MnAl ₅₄ (Ih)	8.19	18.77	3.04	8.31	18.70	2.99	16.50	37.47	6.03
MnAl ₃₂ (DI)	14.70	1.00	4.31	14.39	0.20	1.41	29.90	1.20	5.72
MnAl ₄₄ (DI)	19.37	2.64	3.00	19.13	2.96	2.91	38.50	5.55	5.91

edge of the unit cell. However, for the final densities of states we used 64 K points in the Brillouin zone, which simulates quadrupling of the edge of the unit cell.

In Table I, we give the local magnetic moment on the Mn site in MnAl _{n} clusters based on different theoretical schemes. For the cluster calculations, the Mn-Al distance was optimized via total energy calculations at smaller sizes (MnAl₁₂). For larger clusters, the Mn-Al separation was kept equal to this optimized value. We notice from Table I that the Mn atoms in small MnAl _{n} clusters have a finite moment. This is borne out by experiments⁶ which indicate that Mn _{x} Al_{1- x} QC's have magnetic Mn sites for $x > 5\%$. As the cluster size is increased, the moment decreases. However, the rate of decrease depends on the symmetry. Finally the moment disappears as we approach a size of MnAl₅₄. This size corresponds to a Mn concentration of $\sim 2\%$ and our findings are consistent with experiments⁶ on Mn _{x} Al_{1- x} alloys. The cluster results for MnAl₅₄ are in quantitative agreement with supercell band-structure results giving us additional confidence on our cluster results.

We now compare our results with those of McHenry *et al.*⁷ in more detail. These authors used a 33-atom cluster and found a moment of $3.6\mu_B$ on the Mn site compared to a value of $2.9\mu_B$ obtained by us. They argue that there is an incommensurability between the icosahedral (Ih) symmetry and the d orbitals. Consequently, the Mn d orbitals do not mix with Al p orbitals, which results in a large density of d states at the Fermi energy (E_F) and hence leads to magnetic Mn sites in keeping with the Stoner criterion. While this may be true at small sizes, our results on MnAl₄₄ show that there is an enhanced mixing between Mn d and Al sp orbitals as the size is increased and it is this mixing which quenches the Mn moment. To show the evolution of this mixing with cluster size we carried out a standard group theoretical analysis of the electronic orbitals in cuboctahedral (Oh) and icosahedral (Ih) symmetries. For the Oh symmetry, the electronic orbitals containing Mn d and Al sp states transform according to t_{2g} and e_g representations. On the other hand, electronic orbitals coupling Mn d and Al sp states transform according to fivefold degenerate H_g irreducible representation for icosahedral clusters. In

Table II, we give the spin-up, spin-down, and the total s , p , and d charge contained in states transforming according to t_{2g} and e_g for Oh, and according to H_g for Ih clusters, obtained via a Mulliken population analysis of the orbital charges. A comparison of Table I and Table II shows that the net moment on Mn sites depends on the strength of p - d mixing. For each symmetry, the smaller clusters MnAl₁₂ (Oh), MnAl₁₂ (Ih), and MnAl₃₂ (DI) have smaller p charges and consequently show larger Mn moments. As the cluster size is increased, the amount of p charge increases and there is a corresponding decrease in the Mn moment. A comparison of clusters in Ih and DI symmetries clearly shows the importance of p - d mixing in controlling the moment. MnAl₂₄ (Ih), which allows better mixing between p orbitals of first and second shell with d orbitals of Mn has lower moment than MnAl₃₂ (DI), where mixing between p orbitals of first and second shell is reduced because of the geometry. To summarize this section, we have shown that it is the p - d mixing between Al p and Mn d orbitals which leads to a quenching of the Mn moment. As the cluster size is increased this mixing increases and a single Mn atom surrounded by Al atoms in Oh, Ih, or DI geometries is nonmagnetic.

We next examine the effect of the interaction between Mn atoms on the moment. We have used for this purpose Al _{n} Mn_{55- n} clusters with $n=48, 42, 34$, and 46 . For these clusters, the Mn atoms were distributed in various shells, each cluster had a central Mn site. In

TABLE III. Magnetic moment on Mn at the center and different outside shells in Mn _{m} Al _{n} icosahedral clusters.

Cluster	Center	Shell 1	Shell 2	Shell 3
MnAl ₁₂ (^{Mn₆} _(Al₂₄))Al ₁₂	-0.33		2.24	
MnAl ₁₂ Al ₃₀ Mn ₁₂	0.46			3.89
Mn(^{Mn₄} _(Al₈))(^{Mn₆} _(Al₂₄))Al ₁₂	0.18	0.53	-2.13	
Mn(^{Mn₄} _(Al₈))Al ₃₀ (^{Mn₄} _(Al₈))	-0.11	0.38		-3.62

$\text{Al}_{48}\text{Mn}_7$, the remaining Mn atoms were distributed evenly on the third shell. In $\text{Al}_{42}\text{Mn}_{13}$ cluster, the 12 Mn atoms occupied the outermost shell. In $\text{Al}_{34}\text{Mn}_{11}$, four Mn atoms occupied the second shell and the six occupied the third shell. Finally in the $\text{Al}_{46}\text{Mn}_9$ cluster, four Mn atoms were confined to the second shell and the remaining four to the outermost shell. The corresponding moments on the Mn sites are given in Table III. Note that the moments vary over a wide range depending on the Mn concentration and Mn location. The central moment is coupled either ferromagnetically or antiferromagnetically to other Mn moments. Furthermore, the moments on the Mn steadily increase as the Mn atoms are moved to the exterior region of a cluster.

Unfortunately, the experimental results do not give any quantitative detail on how the moments vary and how the moments depend on the Mn site. What is experimentally established is that there are various Mn moments and that the system resembles a spin glass. Our result in Table III not only confirms the experimental finding but goes a step further in identifying the spatial and concentration dependence of the magnetic behavior of Al-Mn quasicrystals. We hope that this result will be useful in analyzing future experiments and characterizing the magnetism of quasicrystals.

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