Magnetism in Al(Si)-Mn Quasicrystals and Related Phases

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An extreme sensitivity of the magnetic properties to the atomic structure has been observed in Al(Si)-Mn and Al-Pd-Mn quasicrystals, approximants, and liquids with similar Mn concentrations (of the order of 8%–20%). Here, we show that the effect of the local environment of the Mn atoms is not sufficient to explain this complex behavior. A new model is presented, which, taking into account Mn-Mn interactions mediated by the conduction electrons over large distances (5 Å and more), allows one to understand why only a small fraction of the Mn atoms carry a localized magnetic moment in quasicrystals and why a large proportion is magnetic in liquids.

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Quasicrystals [Al(Si)-Mn, Al-Pd-Mn, Al-Cu-Fe, etc.], as well as their periodic approximants, exhibit anomalous electronic and magnetic properties (Refs. [1–3] and references therein). A diamagnetic susceptibility has been measured at room temperature in stable quasicrystals Al-Cu-Fe and Al-Pd-Mn with low Mn content (less than 7%). But in metastable Al(Si)-Mn quasicrystals, in stable Al-Pd-Mn quasicrystals (with Mn concentration larger than 8%), and in some stable approximants (μ Al_4Mn, Mn-rich Taylor phase, and 1/1 Al-Pd-Mn-Si) the presence of a small Curie-like contribution shows that a few percent of the Mn atoms are magnetic (i.e., with localized magnetic moment). In contrast there is no magnetic Mn in most crystalline phases (G $Al_{12}Mn$, o Al_6Mn, α $Al_{73}Si_{10}Mn_{17}$, β Al_9SiMn_3, Al_3Mn), and there is a large proportion of magnetic Mn in the liquid state above the melting point of crystals and quasicrystals [4]. These experimental studies show that the magnetic state of Mn atoms in the Al(Si) host depends strongly on the atomic structure, and that it is influenced by the quasiperiodicity. However, the relevant parameters which govern the formation of localized magnetic moments are still undetermined in theses materials.

Up to now, most of the theoretical studies have focused on the role of the local environment of the Mn atoms to explain the occurrence of localized magnetic moment. In particular, clusters calculations have shown that the local symmetry [5] and the first neighbor distance [6] can have a strong influence. Vacancies, Mn pairs, triplets, or quadriplets are also often invoked to explain magnetic moments [7,8]. However, in crystal and quasicrystal, most of Mn atoms are nonmagnetic in spite of various environments including Mn pairs, triplets, and quadriplets.

More recently, some theoretical works have focused on the occurrence of local moments in a series of Al-Mn alloys [9,10]. The authors conclude that the crystal Al_6Mn is nonmagnetic because of a pseudogap in the local density of states (DOS) at the Fermi energy which is of a Hume-Rothery type. Because of the chemical disorder, a solid solution at the same concentration (on an Al fcc lattice without relaxation) presents a very different electronic DOS, without a pseudo-gap at the Fermi energy [10]. In this solution the Mn atoms are magnetic. It is now well known that the Hume-Rothery pseudogap contributes to the stabilization of crystals, such as Al_6Mn, $Al_{12}Mn$ [11], and quasicrystals (see, for instance, Refs. [10,12] and references therein). Thus the magnetic state of Mn atoms is related to the stabilization mechanism.

Besides, it has been shown that the diffraction of *sp* states by the *d* orbitals of the transition atoms is the main cause for the formation of the Hume-Rothery pseudogap [11]. In the real space, that can be viewed as an effective Mn-Mn interaction mediated by the conduction electrons. Considering the case of nonmagnetic Mn atoms, Zou and Carlsson [13] showed that this interaction strongly contributes to the alloy energy (at constant volume) and that it leads to a preferred Mn-Mn distance of ~4.7 Å. Therefore, to analyze the magnetism of quasicrystals and related phases we have to take into account this effective interaction over a large distance (up to 5 Å and more). Here we show that this interaction depends on the magnetic moments. We calculate it and we show, for the first time, that the large Mn-Mn distance is a crucial parameter for the occurrence of localized magnetic moments in these systems.

In the first part, we briefly present self-consistent calculations of the electronic magnetic structure that we performed by using the linear muffin-tin orbital (LMTO) method [14] in the atomic sphere approximation (ASA). These calculations are based on local density approximations and do not treat the screening of magnetic moments by the Kondo effect. In spite of that, they bring important insight in the understanding of the occurrence of magnetic moments localized on certain Mn atoms. Then we derive our model for the effective Mn-Mn interaction including magnetic effects. One of the most important results of this model is the correlation between the energetically stable positions for the Mn atoms and the inhibition of their magnetic moment. Finally we analyze the value of this medium range interaction in several phases and we obtain an excellent agreement with both the experimental measurements and the self-consistent LMTO calculations.

Before analyzing the medium range Mn-Mn interaction effect in the Al(Si) host, one has to consider the impurity case. In spite of extensive experimental [7,15] and theoretical [5,6,16,17] studies, it is still unclear whether Mn impurity is magnetic or not. Using the LMTO-ASA method, we calculated the moment on an Mn atom substituting an Al in the Al fcc lattice (without interatomic distance relaxation). For the concentration $Al_{107}Mn$, Mn is found magnetic with a $1.8\mu_B$ moment and the gain in energy for the atom to become magnetic is $E_1(1.8\mu_B) \simeq -0.05$ eV per Mn atom. It is instructive to compare this result with the case of $Cu_{107}Mn$ (Mn substituting a Cu in the Cu fcc lattice without relaxation). In that case, Mn is also magnetic, with a $3.4\mu_B$ moment, but $E_1(3.4\mu_B) \simeq -0.7$ eV. The small magnetic energy of the Mn impurity in an Al matrix shows that Mn is close to the magnetic transition. This energy will also depend on the local geometry of Al atoms around the Mn atom. In particular, if interatomic distance relaxation is considered, one expects that the tendency to form a magnetic moment is smaller [6].

For finite Mn concentration the situation is different. To illustrate that we analyze the case of the crystal β Al_9Mn_3Si. Its hexagonal cell contains [18] two isolated Mn triplets distant of about 5 Å. As explained in the introduction, some authors consider that Mn triplets tend to be magnetic. Yet, experimental measurements give nonmagnetic Mn triplets [2]. Our LMTO-ASA electronic structure calculation for β Al_9Mn_3Si confirms the nonmagnetic state of the isolated Mn triplets. In order to determine the role of the effective Mn-Mn interaction on this result, we performed a calculation for the hypothetical β $Al_9Mn_{1.5}Cu_{1.5}Si$ phase, constructed from β Al_9Mn_3Si by replacing one Mn triplet by a Cu triplet in each cell. The Cu has no long-range interaction as its d orbitals are full and it has almost the same number of valence (sp) electrons as Mn. Thus the Fermi energy is essentially unchanged as well as the local environment of the Mn triplet. Yet the LMTO-ASA results show a magnetic moment equal to $\sim 1\mu_B$ on each Mn in β $Al_9Mn_{1.5}Cu_{1.5}Si$ (the 3 Mn in a triplet are almost equivalent with a ferromagnetic spin orientation). This is a proof that the magnetic state of an Mn atom is sensitive to Mn atoms at a distance of ~ 5 Å. The energy of formation of magnetic moments in β $Al_9Mn_{1.5}Cu_{1.5}Si$ is -0.046 eV per triplet.

We now present our model which is a generalization for the magnetism of that of Zou and Carlsson [13] for the structure. We consider Mn atoms with magnetic moments μ in a jelliumlike medium. Let us note that $E_1(\mu)$ is the energy for an isolated atom. By convention we choose $E_1(\mu = 0) = 0$. For a finite, but sufficiently small concentration of atoms we look for the alloy energy, at constant volume, in the form

$$E = \sum_i E_1(\vec{\mu}_i) + \sum_{\langle i,j \rangle} E_2(r_{ij}, \vec{\mu}_i, \vec{\mu}_j) \ldots, \tag{1}$$

where $r_{ij} = |\vec{r}_j - \vec{r}_i|$ is the distance between the Mn atoms i and j. In the limit of small moments, the interaction energy of the two Mn atoms separated by a distance r can be written as

$$E_2(r, \vec{\mu}_1, \vec{\mu}_2) = a(r) + \frac{b(r)}{2}(\mu_1^2 + \mu_2^2) + c(r)\vec{\mu}_1 \cdot \vec{\mu}_2 \ldots . \tag{2}$$

This form is the most general one corresponding to a development up to the second order with respect to $\vec{\mu}_1$ and $\vec{\mu}_2$. It assumes that the Hamiltonian is invariant by rotation in the spin space and that the atoms are identical. In our model we checked that the above development is good for moments smaller than $2.5\mu_B$. $a(r)$ is the potential energy between two nonmagnetic Mn atoms at distance r (when the two atoms are not nearest neighbors). $c(r)$ corresponds to a RKKY interaction between moments. $b(r)$ plays a central role in our study of the condition of formation of local magnetic moments. Even if atom 2 has a zero moment it modifies the electronic structure around atom 1 and changes its magnetic energy. Because of $b(r)$, the formation of a moment on an atom is sensitive to the presence of other nonmagnetic Mn atoms.

We briefly describe our variationnal procedure, which is a standard one, for calculating the effective interaction $E_2(r, \vec{\mu}_1, \vec{\mu}_2)$. From E_2, one calculates the coefficients $a(r)$, $b(r)$, and $c(r)$ by using Eq. (2). We consider two Mn atoms with d orbitals coupled to free states (Al and Si states mainly). Within a mean-field approximation the electronic energy of the system E_{var} is written as

$$E_{\text{var}} = \langle H_{\text{var}} \rangle - \sum_{i=1,2} [E_{di} n_{di} + \Delta_i \mu_i + E_I(n_{di}, \mu_i)], \tag{3}$$

where H_{var} is a variational Hamiltonian of independent electrons, n_{di} and E_{di} are, respectively, the number of d electrons and the on site d energy for atom i. The variational parameters are the magnetic splitting Δ_i as well as the directions for quantization of spin (which are not necessarily the same on all atoms). Note that the five d orbitals are degenerate [11]. The parameter E_{di} is considered as fixed, equal to its value in the nonmagnetic state. $\langle A \rangle$ is the average value of the operator A in the ground state of H_{var}. The interaction energy on each transition atom is represented by a function $E_I(n_d, \mu)$ of n_d and μ. In our variational procedure we consider first the atoms infinitely far apart. Then the two atoms are displaced with Δ_i constant (and thus function of $\vec{\mu}_i$). Using the Hellmann-Feynmann theorem it is easily shown that to first order in $d\mu/\mu$ and dn_d/n_d: $dE_2(r, \vec{\mu}_1, \vec{\mu}_2) = d\langle H_{\text{var}} \rangle$. We have also checked that during this displacement the variations of n_{di} and μ_i are very small.

Thus the interaction energy of two Mn atoms in Al host is

$$E_2 = \int^{E_F} (\epsilon - E_F)[\Delta\rho(\epsilon) - 2\Delta\rho_0(\epsilon)]\,d\epsilon\,, \qquad (4)$$

where $\Delta\rho$ and $\Delta\rho_0$ are, respectively, the variation of the DOS due to the 2 Mn atoms with respect to free electrons DOS, and the variation of the DOS due to one Mn atom (virtual bound state). $\Delta\rho$ is calculated using the Lloyd formula from the transfer matrix T of the 2 Mn atoms in the Al host [19]. The only parameters are the Mn-Mn distance, and the phase shift $\delta_\sigma(\epsilon) = -\tan^{-1}\{(\Gamma/2)/(\epsilon - E_{d,\sigma})\}$, ($\sigma$ is the spin), due to the potential of one Mn atom. δ_σ is determined with the following values in agreement with *ab initio* electronic calculations for Al(Si)-Mn alloys [11,12]: $E_F = 11.7$ eV, $n_d = n_{d\uparrow} + n_{d\downarrow} = 5.8$ electrons per Mn, and $\Gamma = 2.7$ eV. For reasons detailed elsewhere [19], we expect that the calculation of E_2 is valid for not too small distances (greater than 2–3 Å).

The interaction (Fig. 1) has a long-range nature and because of the sharp Fermi surface of Al, it oscillates (Friedel oscillations). When Mn are nonmagnetic, the interaction energy is equal to $a(r)$ which is close [19] to the result of Zou and Carlsson [13].

Let us consider the typical magnetic energies that result from the interaction $b(r)$. For a moment μ in the presence of N nonmagnetic atoms at a distance of ~5 Å the change of energy is about $0.05(N/4)(\mu/2)^2$ eV. If there are several atoms at this distance and for a localized magnetic moment $\mu \simeq 2\mu_{\mathrm{B}}$ this is quite comparable to a typical magnetic energy E_1 of an isolated Mn atom. This result confirms our previous conclusions that the effective Mn-Mn interaction can modify the magnetic state of Mn atoms even for distances of ~5 Å and more.

A remarkable feature displayed by Fig. 1 is the correlation between the minima (respectively, maxima) of $a(r)$ (the interaction energy of the nonmagnetic state) and the maxima (respectively, minima) of $b(r)$ and $c(r)$. The general trend is that in the magnetic state the absolute value of the interaction energy is decreased. As a consequence we expect that atoms in a negative energy site (stable position) tend to be nonmagnetic due to the interaction with other nonmagnetic Mn atoms.

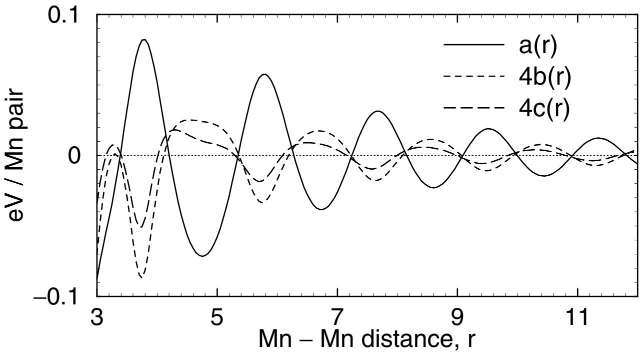

FIG. 1. Coefficients $a(r)$, $b(r)\mu^2$, and $c(r)\mu^2$ ($\mu = 2\mu_{\mathrm{B}}$) of the Mn-Mn interaction E_2 [see Eq. (2)]. r is in Å.

We come now to an analysis of the medium range magnetic interaction in several phases. For real alloys the scattering of electrons by static disorder or by phonons leads to a finite mean-free path L_0. The interaction between atoms separated by a distance smaller than L_0 will be affected by the scattering. When considering the average interaction between atom 1 with all atoms at a distance r this leads to an exponential damping on a typical distance L_0. The value of L_0 is difficult to estimate and depends on structural quality and temperature. For this reason we plot the results as a function of L_0 in the range $3 \le L_0 \le 40$ Å. The estimate of the maximum value of L_0 at room temperature or even below is reasonable in view of the measured resistivities of Al-Mn alloys with a small proportion of Mn [20]. The smallest value of $L_0 \simeq 3$ Å can probably be realistic only in the liquid phase.

We are interested in the formation of a moment on a local entity which can be an isolated Mn atom, a pair, or a triplet. The magnetic energy can be written,

$$\Delta E \simeq E_1(\{\mu_i\}) + \sum_i \mathcal{B}_i \mu_i^2; \qquad \mathcal{B}_i = \sum_j \frac{b(r_{ij})}{2}\, e^{-\frac{r_{ij}}{L_0}}. \qquad (5)$$

$E_1(\{\mu_i\})$ is the magnetic energy of the isolated entity and the sum $\mathcal{B}$ includes only the contribution from Mn atoms that do not belong to the pair or triplet.

In $Al_{12}Mn$ [11], Al_6Mn [11], and α AlSiMn [12], all Mn sites are equivalent and the Mn atoms are not first neighbor. The corresponding $\mathcal{B}(L_0)$ [Fig. 2(a)] is always positive. Assuming $|E_1(\mu_i)| \le 0.05$ eV for $\mu \simeq 2$ as discussed above, this criterion leads to nonmagnetic Mn in these phases, as confirmed by LMTO calculations [10–12].

Figure 2(b) displays the value of $\mathcal{B}$ for β Al_9Mn_3Si and for the fictitious β $Al_9Mn_{1.5}Cu_{1.5}Si$. Both terms are positive but $\mathcal{B}(\beta\, Al_9Mn_3Si) \gg \mathcal{B}(\beta\, Al_9Mn_{1.5}Cu_{1.5}Si)$. This shows that the Mn-Mn intertriplet interaction maintains the Mn triplet nonmagnetic in β Al_9Mn_3Si whereas this intertriplet interaction is very small for β $Al_9Mn_{1.5}Cu_{1.5}Si$ which explains the occurrence of magnetic triplets.

Figure 2(c) displays the values of $\mathcal{B}$ for the ten inequivalent Mn sites of the μ Al_4Mn approximant [21]. Mn(4), Mn(8), and Mn(10) form triplets similar to the triplets in the β phase. As $\mathcal{B}_{\mathrm{Mn}(4)}$, $\mathcal{B}_{\mathrm{Mn}(8)}$, and $\mathcal{B}_{\mathrm{Mn}(10)}$ have the same order of magnitude as $\mathcal{B}_{\mathrm{Mn}}$ in the β phase (Fig. 2), one expects that Mn triplets in the μ phase are also nonmagnetic. Quite remarkably $\mathcal{B}_{\mathrm{Mn}(1)}$ decreases when L_0 increases whereas all the other $\mathcal{B}$ ($\mathcal{B}_{\mathrm{Mn}(2)}$ to $\mathcal{B}_{\mathrm{Mn}(9)}$) increase when L_0 increases. For $L_0 > 9$ Å, $\mathcal{B}_{\mathrm{Mn}(1)}$ is negative which favors a stable magnetic Mn(1) (Wyckoff site 2a in [21]). Indeed it has been recently suggested experimentally [2] that Mn(1) is magnetic. Note that the local environment around Mn(1) (several vacancies) could also contribute to the occurrence of the magnetic moment. The structure of the μ approximant is closely related to the quasicrystals, and one can expect that a small fraction of Mn sites in quasicrystals, similar to Mn(1) in μ Al_4Mn, are magnetic when most of Mn atoms are nonmagnetic.

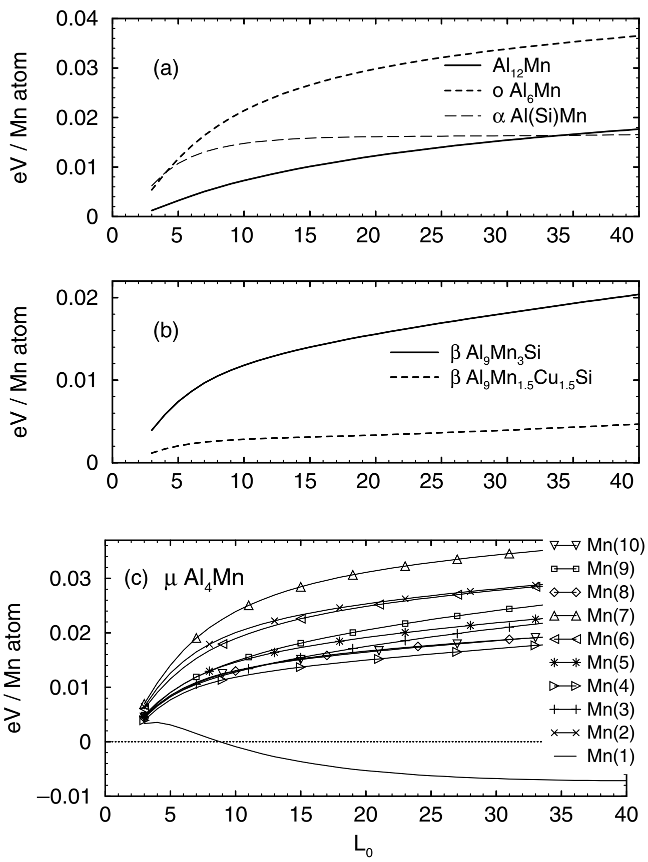

FIG. 2. $\mathcal{B}(L_0)$ for several phases (see text). L_0 is in Å.

The case of the liquids obtained from the melting of crystals and quasicrystals is different. The lost of the medium range order and the small value of the mean-free path (typically a few interatomic distances) lead to $\mathcal{B}$ very close to 0. The situation is almost equivalent to the impurity case, for which Mn are close to the magnetic transition. Yet several effects could play a role. The thermal expansion increases the average distance between a Mn atom and its Al neighbors which should favor a magnetic state. Moreover, displacements of the atoms are important. Consequently, the magnetic moment may change rapidly with the change of the atomic position. There should also be spin fluctuation due to temperature since the thermal energy kT is comparable to the typical magnetic energy 0.05 eV. All these elements should favor the occurrence of a finite average square moment on Mn in the liquids as it has been found experimentally [4] and from calculations [9,10].

To conclude let us recall that the formation of localized magnetic moments in Al(Si)-Mn quasicrystals and related phases has been much debated in terms of local symmetry, vacancies, and pairs or triplets of Mn atoms. Here, we have shown for the first time, that an effective Mn-Mn interaction mediated by the conduction electrons plays a major role on the magnetic properties of these alloys. The distance between the Mn atoms (as large as 5 Å or more) has been shown to be an essential parameter for the occurrence of the magnetism on these Mn. As the Mn-Mn interaction is intimately related to the emergence of quasiperiodicity, our work shows that the occurrence of localized magnetic moments is intrinsically linked to the stability of these materials.

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