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Origin of magnetism in crystalline and quasicrystalline AlMn and AlPdMn phases

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The existence of localized moments on a small fraction of the Mn atoms in the μ -Al₄Mn_xCr_{1-x} hexagonal phase, closely related to AlMn quasicrystals, is shown by magnetization and nuclear magnetic resonance studies. Deviations from a Curie behavior observed in the μ phase, as well as in the AlMn, AlMnSi, and AlPdMn quasicrystals, can be interpreted by a Kondo effect. The crystallographic site leading to magnetic Mn in the μ phase is identified and the moment formation is justified by theoretical calculations. These results shed light on the origin of magnetism in quasicrystalline phases where a similar site must also exist.

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The atypical electronic properties of quasicrystalline (QC) phases, reduced density of electronic states (DOS) at the Fermi level, as well as anomalous transport properties, have attracted much attention.^{1,2} We will focus here on their magnetic properties which remain poorly understood. Whereas most of the QC phases are nonmagnetic, Curie terms are detected in the metastable icosahedral and decagonal AlMnSi and AlMn phases and in the stable AlPdMn icosahedral phases.^{3,4} Most of the studies suggest that only a few Mn atoms are magnetic³⁻⁵ in contrast to liquids in equilibrium with these QC phases where a large proportion of the Mn atoms carries a localized moment.⁶ In solid phases the fraction of magnetic Mn increases very rapidly with increasing Mn composition.⁷ The similarity between metastable AlMn phases which are strongly disordered and stable AlPdMn phases which have a very high structural quality without phason disorder, suggests that defects are not the main origin of magnetism. Several theoretical approaches have pointed out the influence of the pseudogap in the DOS at the Fermi level and of the hybridization between the Al *p* and the Mn *d* states on the moment formation on Mn

atoms.^{8,9} In addition the Mn-Mn distances should be considered because the effective Mn-Mn pair potential, strong up to 10 Å in AlMn phases,¹⁰ depends on the magnetic state of the Mn atoms.¹¹ The first neighbor environment should also be analyzed because the moment depends on the transition metal-Al distance.¹² However the application of these theoretical predictions to QC phases was hindered by the absence of identification of the magnetic sites. Thus it is worth examining whether AlMn or AlPdMn intermetallic phases, with compositions close to those of quasicrystals, would exhibit similar magnetic properties. No localized moments are present in the periodic Al(Si)Mn phases which have been studied up to now: Al₆Mn, β -Al₉Mn₃Si and α -Al_{72.4}Mn_{17.5}Si_{10.1} phase which is a cubic approximant.³ Approximants are periodic phases with a large unit cell exhibiting a local chemical, and electronic, order very close to that of QC.² Thus it is puzzling to observe that the magnetic properties of the α phase which exhibits a high resistivity and a pseudogap at E_F (Ref. 13) differ from those of QC. In the present work, by combining magnetization and nuclear magnetic resonance (NMR) studies, we show that localized

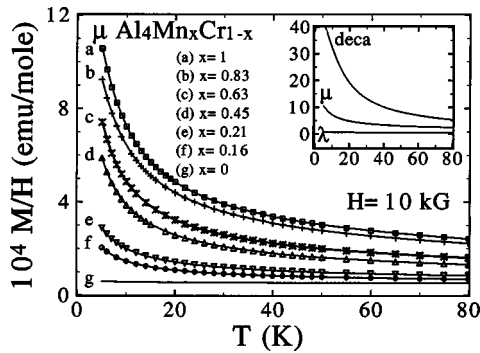


FIG. 1. Temperature dependence of the susceptibility (M/H in emu/mole sample) for the $\text{Al}_4\text{Mn}_x\text{Cr}_{1-x}$ μ compounds. (All the data were not drawn for the sake of clarity.) Inset: μ Al_4Mn [sample (a)], decagonal Al_4Mn and λ $\text{Al}_{4.5}\text{Mn}$ phases.

moments are present on a small fraction of the Mn sites in the hexagonal μ - Al_4Mn phase.¹⁴ We shall discuss magnetic properties of this phase and compare them to those of quasicrystals.

Ternary $\text{Al}_4(\text{Mn}_x\text{Cr}_{1-x})$ μ compounds [with $x = 1, 0.83, 0.63, 0.45, 0.21, 0.16, 0$ in samples (a) to (f), respectively] were elaborated by Bridgman growth.^{15,16} It was shown by neutron diffraction that the Mn/Cr substitution is isomorphic in the μ phase.¹⁵ The x values, determined by electron probe microanalysis, are average values over the Mn/Cr ratio gradients through the ingot length. A few percent of secondary phases of the type Al_6Mn or Al_7Cr was detected at grain boundaries of μ -phase samples. These phases are nonmagnetic and do not affect the magnetic measurements presented below. In all samples containing Mn, an increase of the magnetization [measured in a field of 10 kG in the range (5–200 K)] is observed with decreasing temperature (Fig. 1). The μ - Al_4Mn phase is less magnetic than the decagonal Al_4Mn phase (inset of Fig. 1). The magnetization decreases progressively when Mn is replaced by Cr and the μ - Al_4Cr phase exhibits a temperature independent susceptibility. Thus Cr atoms carry no localized magnetic moments in the μ phase. Curie-Weiss fits of the form $\chi = \chi_0 + C/(T + \Theta)$ can only be performed over a limited temperature range [here, χ_0 is the temperature independent susceptibility and C the Curie constant, $C = c^* g^2 \mu_B^2 N_a S(S+1)/3k_B$ with c^* the concentration of magnetic Mn]. The fit parameters strongly depend on the chosen temperature range. For example in the μ - Al_4Mn phase one gets $c^* S(S+1) = (1.45 \pm 0.13) 10^{-2}$ (with $g=2$),

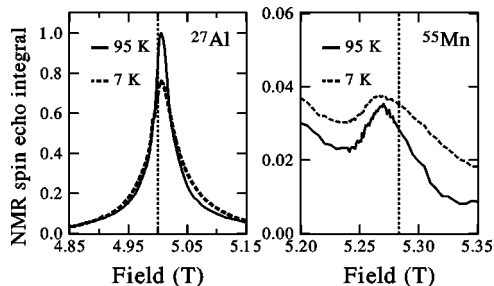


FIG. 2. ^{27}Al and ^{55}Mn NMR spectra versus field at 95 K and 7 K in $\mu\text{Al}_4\text{Mn}_{0.83}\text{Cr}_{0.17}$ sample at a constant frequency $\nu_0 = 55.47$ MHz. The reference fields (ν_0/γ_n , with γ_n the gyromagnetic factor) are indicated by vertical lines.

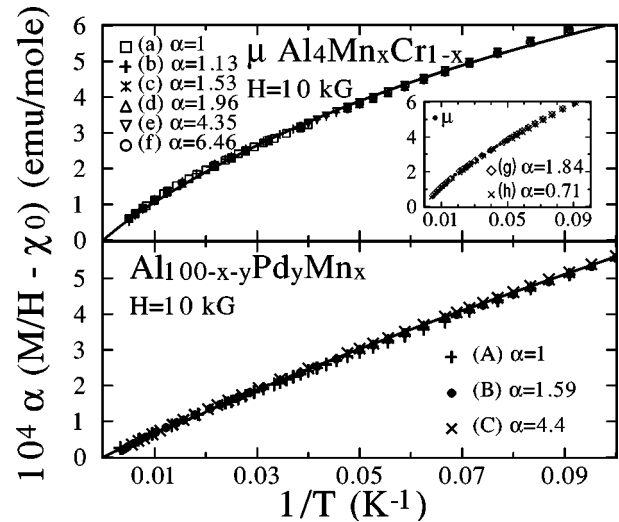


FIG. 3. Susceptibility vs $1/T$ in μ - $\text{Al}_4\text{Mn}_x\text{Cr}_{1-x}$ phases (top) and in $\text{Al}_{100-x-y}\text{Pd}_y\text{Mn}_x$ quasicrystals (bottom). In each case, the data for a given sample are multiplied by a factor α so that all the susceptibility curves coincide. (All the data were not drawn for the sake of clarity.) The solid lines are Kondo susceptibility for $T_K = 5.3$ K (top) and $T_K = 0.7$ K (bottom). Inset: the decagonal $\text{Al}_{0.8}(\text{Mn}_{0.3}\text{Fe}_{0.35}\text{Cr}_{0.35})_{0.2}$ [sample (g)] and the icosahedral $\text{Al}_{0.73}(\text{Mn}_{0.3}\text{Fe}_{0.35}\text{Cr}_{0.35})_{0.21}\text{Si}_{0.06}$ [sample (h)] phases are compared to the μ compounds after appropriate scaling.

$\Theta = (3.5 \pm 0.4)$ K, $\chi_0 = (1.7 \pm 0.08) 10^{-4}$ emu/mole in the range (10–40 K) and $c^* S(S+1) = (2.08 \pm 0.13) 10^{-2}$, $\Theta = 0$, $\chi_0 = (1.12 \pm 0.04) 10^{-4}$ emu/mole in the range (80–200 K). In a given temperature range, the Curie constant is found to decrease linearly with the Mn content. Assuming that all the Mn atoms are magnetic and have the same spin, extremely small spin values are obtained ($S \leq 0.1$). It seems therefore reasonable to consider that only a few Mn atoms carry a magnetic moment. Such an assumption is confirmed by the detection of a ^{55}Mn NMR signal, as illustrated in Fig. 2 for sample (b). As in AlMn QC,⁵ this signal reveals the existence of nonmagnetic Mn atoms.¹⁷ In all samples containing Mn the width of the ^{27}Al and ^{55}Mn NMR spectra increases with decreasing temperature, as can be seen in Fig. 2 for sample (b). This magnetic broadening effect¹⁸ results from the coupling of the Mn magnetic moments with the Al nuclei (and with the Mn nuclei on nonmagnetic Mn sites) through the polarization of the conduction electrons and shows that the magnetic Mn are homogeneously diluted in the μ phase and are therefore an *intrinsic* feature of this structure.

As mentioned above, a Curie, or Curie-Weiss, law cannot account for the susceptibility data. Indeed a plot of M/H versus $1/T$ reveals a continuous curvature. Similar features were observed in $\text{Al}(\text{Si})\text{Mn}$ and AlPdMn quasicrystals^{3,4} and usually ascribed to magnetic interactions. However, for all the μ compounds containing Mn, the susceptibility data, $M/H - \chi_0$, coincide in the range (10–200 K) once multiplied by an appropriate scaling factor α (Fig. 3).¹⁹ The value of $\chi_0 = \chi(1/T \rightarrow 0)$ was determined by extrapolating the data using a polynomial fit. Therefore the anomalous temperature dependence of the susceptibility in the μ - $\text{Al}_4\text{Mn}_x\text{Cr}_{1-x}$ compounds is not due to magnetic interactions but is instead characteristic of a single magnetic atom. The scaling factor α

is found proportional to x which proves that the fraction of magnetic Mn [c^*/c with $c=0.195x$ (Ref. 16)] is independent of x . These results suggest that only one, or at most only a few, crystallographic sites are magnetic in the μ structure and that Cr atoms randomly occupy magnetic and nonmagnetic sites as expected for an isomorphic substitution. The anomalous temperature dependence of the susceptibility can be explained by Kondo coupling between the localized moment with the conduction electron spins.²⁰ Using the analytical results of Ref. 21 for the n channel Kondo model (with $n=2S$) a very accurate fit of the data is obtained: see Fig. 3. Note that the only parameters are the Kondo temperature T_K (between 5.0 and 5.5 K using the T_K definition of Ref. 20) and the fraction of magnetic Mn, $c^*/c=(1.75\pm 0.15)10^{-2}$, which simply determines the vertical scale. The theoretical susceptibility is nearly insensitive to the S value, apart from a scaling factor.²¹ We assumed $S=5/2$ which is the most reasonable value for Mn. Note that this spin value is only reached at very high temperature ($T>10^3T_K$) and that Curie-Weiss fits at lower temperature lead to smaller apparent S values. Indeed, in the μ -Al₄Mn phase, we found $S\sim 2$ in the range $80\leq T\leq 200$ K and $S\sim 1.6$ in the range $10\leq T\leq 40$ K, using the previous c^*/c value. It is interesting to compare these results with susceptibility data in Al(Si)Mn QC phases. We studied decagonal Al_{0.8}[Mn _{x} (Fe_{0.5}Cr_{0.5})_{1- x}]_{0.2} and icosahedral Al_{0.73}[Mn _{x} (Fe_{0.5}Cr_{0.5})_{1- x}]_{0.21}Si_{0.06} phases, with $1\geq x\geq 0$, where Mn atoms are progressively replaced in an isomorphic substitution by nonmagnetic Fe and Cr atoms.²² The susceptibility data for the two samples with the lower Mn content ($x=0.3$) correspond exactly with those of the μ compounds, after appropriate scaling (inset of Fig. 3). For larger x values, deviations occur due to magnetic interactions between Mn atoms: indeed all these samples are more magnetic than the μ -Al₄Mn phase and exhibit spin glass transitions between 1.7 and 5.5 K. In conclusion the temperature dependence of the susceptibility is identical in the μ phase and in the icosahedral AlMnSi and decagonal AlMn phases, provided that magnetic Mn are sufficiently diluted to avoid magnetic interactions. In all these phases the magnetic Mn are affected by a Kondo effect with the very same Kondo temperature. T_K depends on the DOS at E_F : $T_K=D \exp[-1/JN(E_F)]$, where D is an energy cutoff of the order of E_F and J is the exchange coupling between the localized and conduction electron spins.²⁰ Therefore we can conclude that the same kind of magnetic sites exists in all these phases.

Hence it is worth examining the structure of the hexagonal μ phase [$P6_3/mmc$, $a=19.98$ Å, $c=24.673$ Å (Ref. 14)] in order to identify possible magnetic sites. There are 110 Mn atoms distributed on ten crystallographic sites. For nine of these sites, Mn atoms are surrounded either by 11 Al+1 Mn or by 10 Al+2 Mn atoms located at the vertices of distorted icosahedra, in a distance range (2.408–2.874 Å). There is only one Mn site (Wyckoff site $2a$ in Ref. 14) where the Mn atoms are surrounded by 9 Al sites, at 2.359 and 2.409 Å, partially occupied so that the coordinance is about seven atoms. The specificity of site $2a$ in the μ structure led us to suggest that Mn atoms on this site could be magnetic. Then the fraction of magnetic Mn c^*/c would be equal to $2/110$ which is in perfect agreement with the experimental values found above, assuming $S=5/2$. Theoretical

considerations on moment formation energy fully confirm this conjecture. In AlMn phases the condition for the occurrence of a magnetic moment does not depend only on the local properties but also on Mn-Mn distances. The strength of the effective oscillating Mn-Mn pair interaction depends on the magnetic states of the Mn atoms and decreases as Mn spin increases.¹¹ We calculated the variation ΔE of the free energy of the Mn-Mn pair interactions when Mn atoms on a given crystallographic site of the μ phase become magnetic, whereas all the other Mn atoms remain nonmagnetic. According to the ΔE value, one can predict whether Mn atoms are close to a magnetic transition but no information on the actual spin value can be obtained because the effective Mn-Mn pair potential could only be calculated for $S\leq 1$. For all Mn sites, except site $2a$, ΔE is found larger than 0.1 eV (for $S=1$) which shows that the Mn-Mn interactions impede the formation of a local moment. Instead, for site $2a$, ΔE is close to zero. Therefore Mn atoms on this site are not sensitive to Mn-Mn interactions and thus are susceptible to be magnetic. Going further and predicting their magnetic, or nonmagnetic, character requires a detailed formulation of the criterion for moment formation, taking fully into account the electronic structure, which cannot be achieved. But the combination of experimental and theoretical results leads to a coherent picture if Mn atoms on site $2a$ are indeed magnetic in the μ phase. In agreement with this result such a site is not present in the nonmagnetic Al₆Mn, β and α AlMnSi phases. We also studied the cubic G -Al₁₂Mn phase, constituted of a bcc packing of Al₁₂Mn icosahedra, and the ξ' AlPdMn in which the two Mn sites have an icosahedral coordination²³ and found them nonmagnetic. In the hexagonal λ Al_{4.5}Mn phase [$P6_3/m$, $a=28.39$ Å, $c=12.39$ Å (Ref. 24)], a site similar to site $2a$ in the μ phase exists [Mn(1) of Ref. 24]. All the other Mn sites in the λ structure have an icosahedral coordination. Taking into account the Mn-Mn pair potential we found that Mn(1) are the only Mn atoms susceptible to be magnetic ($\Delta E\sim 0$). We elaborated a λ phase sample, by solid state reaction at 680 °C between μ and Al₆Mn phases, and found it nonmagnetic (Fig. 1). The fact that Mn(1) does not carry a localized moment in the λ phase, contrary to Mn($2a$) in the μ phase, suggests that this Mn atom is indeed very close to a magnetic \leftrightarrow nonmagnetic transition. Then a very small difference in the electronic structure of μ and λ phases would be sufficient to modify its magnetic properties.

Experimental results on Al_{100- x - y} Pd _{y} Mn _{x} QC phases reveal a close similarity with AlMn phases. The susceptibility curves measured on three different single crystals coincide after scaling (see Fig. 3). Therefore magnetic interactions cannot explain the observed deviations from a Curie law. The compositions, as determined by electron probe microanalysis, are $x=9\pm 0.4$ in samples (A) and (B), $x=8.6\pm 0.4$ in sample (C) and $y=22.8\pm 0.3$ in the three samples. An excellent fit of the susceptibility data can be obtained in a Kondo model with $T_K=0.7$ K and $c^*/x=1.910^{-3}$ in sample (A). Contrary to the case of the μ phases, c^*/x is found to vary rapidly with x in agreement with the results of Ref. 7. Note that the change of T_K , from 5.3 K in AlMn QC phases to 0.7 K in AlPdMn QC phases, corresponds to a variation of only 20% of $JN(E_F)$. Therefore magnetic Mn is in a very similar state in AlMn and AlPdMn QC despite the

change in T_K . This similarity is striking when taking into account the large difference in the average $N(E_F)$ values as deduced from the electronic specific heat coefficient [$\gamma \sim 10$ mJ/(mole.K²) in AlMn QC and ≤ 0.5 mJ/(mole.K²) in AlPdMn QC (Refs. 3 and 4)]. This observation suggests that a local DOS should be considered in Kondo effect as well as for computing Ruderman-Kittel-Kasuya-Yoshida (RKKY) couplings²⁵ which are actually driven by the same parameter $JN(E_F)$. Finally it should be emphasized that a competition between Kondo effects and RKKY interactions occurs in AlMn and AlPdMn QC phases when the number of magnetic Mn increases ($T_K = 5.3$ K in AlMn QC while the spin glass temperature is equal to 4.2 K in decagonal Al₄Mn). It is interesting to note that the T_K values in AlMn and AlPdMn QC phases are in between those in dilute CuMn and AlMn alloys (10 mK and ~ 600 K, respectively^{20,26}). In dilute alloys one of the best signatures of a Kondo coupling is the existence of logarithmic increase of the resistivity at low temperature. In AlMn and AlPdMn QC phases, despite the

very high resistivity characteristic of the quasiperiodic state, such upturns seem to be detected.^{3,27}

In conclusion, a coherent picture of magnetic properties of AlMn and AlPdMn periodic and quasicrystalline phases can be drawn from these results. Most of the Mn atoms do not carry a localized moment. Moments appear on peculiar sites with a local density of states which can be quite different from that on the other Mn atoms. Magnetic Mn are in a very similar state in the μ Al₄Mn phase and in AlMn and AlPdMn QC phases and they are coupled with the conduction electrons via a Kondo effect. In the μ phase the magnetic sites occupy a well-defined crystallographic site characterized by a low coordination. The observed similarity between the magnetic properties of the μ phase and those of AlMn and AlPdMn quasicrystalline phases suggests that such a site exists in QC phases as well.

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