

Magnetic and calorimetric study of a single grain of quasicrystalline Al-Pd-Mn

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We present the magnetic and calorimetric results obtained on a single $\text{Al}_{68.7}\text{Pd}_{21.7}\text{Mn}_{9.6}$ quasicrystal grain. We show that a few Mn's are really magnetic and carry a large spin. These spins are coupled by Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions yielding a spin-glass transition at 1.1 K. Surprisingly, the RKKY potential is found to equal that of metastable Al-Mn quasicrystals and that of crystalline Cu-Mn. In contrast with the case of melt-spun metastable Al-Mn quasicrystals, the linear T term of the specific heat is very small: about 1/4 of that of Al. Finally, we conclude to the general character and to the intrinsic origin of the magnetism of quasicrystals containing Mn.

INTRODUCTION

At the beginning of the quasicrystal (QC) story, many experimental studies were devoted to Al-Mn metastable systems. The results address many new questions about the peculiar magnetism observed in these compounds. But many uncertainties remained about the role of the numerous defects present in the samples, inherent to the method of preparation. Are the defects at the origin of some magnetic properties and of the strong spin-orbit coupling? The discovery of stable Al-Pd-Mn QC's of high structural quality gives the opportunity of answering a central question: What are the specific magnetic properties of a QC structure containing d elements and especially Mn atoms.

In this Introduction, first we summarize the conclusions of the studies of metastable $\text{Al}_{1-x}\text{Mn}_x$ compounds. For $x > 14$ at. %, three phases can be obtained: (a), (i), and (T). In the amorphous phase denoted (a), a strong chemical local order exists, similar to that of QC's.¹ The (i) phase is a three-dimensional icosahedral QC obtained with the addition of a small amount of Si. In the (T) phase, QC planes are separated periodically. All three phases exhibit the same general behavior: Only a few Mn atoms are magnetic and carry a large effective magnetic moment μ_{eff} . Their number N increases drastically when the concentration x of the Mn atoms increases slightly. These results are deduced from both magnetic and calorimetric measurements. From the magnetization M data obtained in very low fields H , one deduces a very small value of $N\mu_{\text{eff}}^2$. The latter is given by the Curie constant C : $M = CH/T$, where $C = N\mu_{\text{eff}}^2/3k_B$. Other measurements are necessary to give separately N and μ_{eff} . Magnetization data obtained in moderate or large fields give the nonlinear susceptibility χ_3 ($\sim N\mu_{\text{eff}}^4$) and the saturated value of M ($M_{\text{sat}} = N\mu_{\text{eff}}$), respectively. From the Curie constant and one of the previous quantities,

different authors found different but always large values of the moment μ_{eff} in samples containing about 20 at. % Mn: μ_{eff} equals about $2.5\mu_B$ in the early Ref. 2, $4-5\mu_B$ in Ref. 3, or $7\mu_B$ in Ref. 4. One can deduce a value of the spin S putting $M_{\text{sat}} = NgS$, the validity of taking μ_{eff}^2 proportional to either $S(S+1)$ or to S^2 in the Curie constant is discussed later in Sec. II. It remains that the value of μ_{eff} is large, which implies a very small value of the number of really magnetic atoms observed in magnetization measurements. But this is not sufficient to prove that only a few Mn atoms are really magnetic. Most of the magnetic Mn moments could be strongly correlated in such a way that they give no contribution to the magnetization. It is the case of antiferromagnetic pairs. The hyperfine contribution C_N of the specific heat is a good local probe to give the total number N' of the really magnetic Mn atoms. Below 300 mK, C_N is sizable and is proportional to S^2/T^2 per magnetic Mn atom, whatever the magnetic interactions between the electronic spins S of the Mn atoms are. One measures the total contribution giving $N'S^2$. The value of $N'S^2$ is also very small and it is very close to that given by the Curie constant determined on the same sample. Once the conclusion is established that most of the Mn atoms are not magnetic, a new question arises about the origin of the lack of magnetism of these Mn atoms. An early explanation was given in terms of a virtual bound-state model. It was known that a single Mn atom in a crystalline matrix of Al is of the Kondo type, i.e., exhibits no moment up to 1000 K. In addition, the linear T term of the specific heat of the (a), (i), and (T) phases is very large, supporting the idea of an enhancement of the density of states at the Fermi level due to a virtual bound state.⁵ In addition, a very large spin-orbit coupling was evidenced from the observation of a huge anomalous Hall resistivity proportional to the magnetization.⁶ This could be attributed either to the presence of numerous defects or to the QC structure.

Here we present our results obtained on a single Al-Pd-Mn quasicrystal following the same method of investigation as that expressed above for metastable Al-Mn QC's. In Sec. I, we give some details about our experimental setup. We also show that there exists a Mn concentration gradient along the axis of crystal extraction of our single grain. In Sec. II, we estimate the number and the magnetic moment of the magnetic Mn atoms observed in magnetization measurements. In Sec. III, we analyze our specific heat data obtained down to 70 mK: They confirm the general behavior of QC's containing Mn atoms, except about the value of the linear T term, which is very small in the present case. In Sec. IV, we show that the spins of the magnetic Mn atoms are coupled by Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, involving a potential energy that equals that of metastable Al-Mn compounds. Finally, in Sec. V, we discuss the very general behavior of the magnetism of all the QC's containing Mn. We state that this magnetism is not related to random defects of the structure due to the preparation.

I. SAMPLES AND EXPERIMENTAL SETUP

Most of the work presented here is devoted to the study of a single QC grain of Al-Pd-Mn. It is about 1.5 cm long and 0.5 cm large with the two faces perpendicular to a twofold axis noted A_2 in the following. The grain was extracted in the upper part, 2 cm long, of an ingot grown by a Bridgman technique.⁷ The nominal composition of the ingot is $\text{Al}_{69}\text{Pd}_{21.5}\text{Mn}_{9.5}$. Just above the grain, the electron probe analysis gives a composition $\text{Al}_{68.7}\text{Pd}_{21.7}\text{Mn}_{9.6}$ (with a precision of 2%). This grain has been extensively characterized by various techniques:⁷ It is of perfect icosahedral symmetry, does not exhibit any phason disorder and no frozen-in strain can be observed within the instrumental resolution. Also, electron microscopy observations did not reveal the presence of any decagonal precipitates. The grain has been investigated previously by different physical techniques, such as acoustic attenuation and sound velocities,⁸ and transport measurements.⁹ In this paper, we report on magnetization, ac magnetic susceptibility and specific-heat measurements.

Using a superconducting quantum interference device (SQUID) magnetometer (Metronique), we measured the magnetization M at different temperatures T (> 1.7 K) in fields up to 8 T on the centimeter size grain. In Fig. 1, we show our data in a M -vs- H diagram at $T = 1.7$ K. Thereafter we have cut a platelet perpendicular to the A_2 axis at the upper extremity of the grain, 0.8 mm thick and 0.112 g in weight. The magnetization per gram of this plate is two times larger than that of the whole grain at any field and temperature (see Fig. 1). We conclude to the existence of a gradient of concentration of Mn along the A_2 axis of the grain. Subsequently, we have cut a small parallelepiped in the middle of the plate. Its magnetization M is close to that of the plate, only 2.5% smaller at 1.7 K (see Fig. 1). It indicates that there is no Mn concentration gradient in the plane perpendicular to the A_2 axis. In the following, we present magnetization

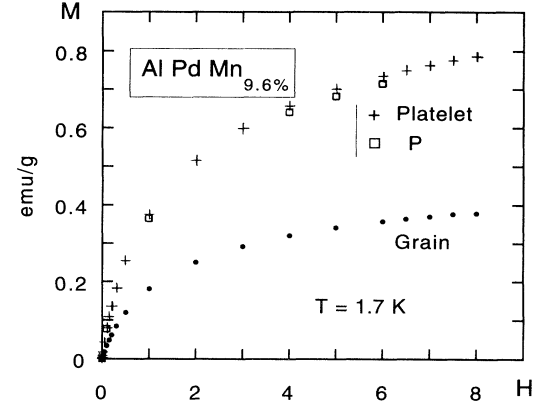


FIG. 1. Magnetization in H up to 8 T, at $T = 1.7$ K, of our single grain of Al-Pd-Mn, of a platelet cut at its upper extremity and of a parallelepiped (P) cut in the middle of the platelet.

and specific-heat data obtained on the platelet of composition 68.7-21.7-9.6.

We present also magnetization data obtained on melt-spun ribbons prepared by the Laboratoire d'Etudes des Propriétés Electroniques des Solides Lab group of Grenoble. The studied samples are of nominal composition $\text{Al}_{70.5}\text{Pd}_{22}\text{Mn}_{7.5}$ and $\text{Al}_{71}\text{Pd}_{18}\text{Mn}_{11}$. Some of our magnetization results on the melt spun alloys were already presented in Ref. 10.

Specific heat measurements were carried out in the T range between 70 mK and 7.5 K with the usual thermal relaxation technique already used for the study of the metastable Al-Mn compounds.^{5,6,11} Due to the very good thermal diffusivity of the single quasicrystalline sample, accuracy of data is excellent especially below 2–3 K, where the contribution of the addenda becomes rapidly negligible. We used a SQUID susceptometer in which a dilution refrigerator is inserted to measure the ac susceptibility in the 50 mK–2 K temperature range with an exciting field of 1 Oe.

II. MAGNETIZATION AND AC SUSCEPTIBILITY RESULTS

In Fig. 2 we show the magnetization M measured up to 8 T at different temperatures. The ac susceptibility data (χ_{ac}) are presented in Fig. 3: χ_{ac} is plotted vs T . It is found to exhibit a maximum at $T_m = 1.195 \pm 0.005$ K when the exciting field is at a frequency of 22 Hz. When a frequency of one decade larger is used (223 Hz), we find the maximum at $T_m = 1.22 \pm 0.01$ K. This very small frequency dependence of T_m cannot be accounted for by an Arrhenius law. It is in agreement with the frequency dependence observed when a spin-glass transition occurs as it is the case in metastable Al-Mn compounds.⁴

Above this temperature, the dc susceptibility χ_{dc} measured in a field of 100 Oe follows a Curie law, $\chi_{dc} = M/H = C/T$: See Fig. 4, where χ_{dc} is plotted vs $1/T$. For a paramagnet or a spin glass $C = N\mu_{eff}^2/3k_B$, where N and μ_{eff} denote the number of magnetic entities and their effective magnetic moment respectively. Here

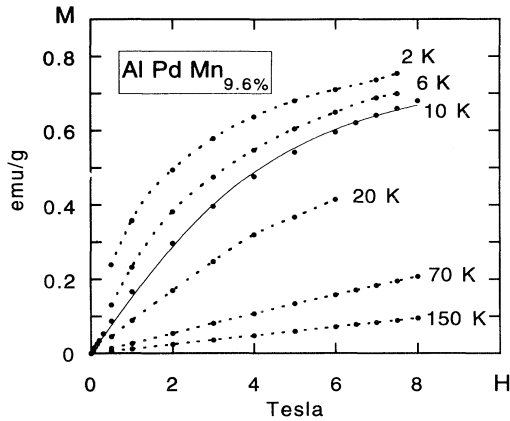


FIG. 2. Magnetization $M(H)$ of the platelet measured at different values of the temperature $T \geq 2$ K. The dashed curves are guides for the eyes. The full curve is given by the Brillouin function with $S=3.3$, which provides the best fit of the magnetization at 10 K.

we find $C = 1.6 \times 10^{-4}$ emu/g = 7.5×10^{-3} emu/mol. At this step, we note that we should find a value of C equal to 64×10^{-4} emu/g if all the Mn atoms were magnetic, each of them carrying a moment of $5\mu_B$. To obtain separately N and μ_{eff} , we try to evaluate the value of the saturated magnetization $M_{\text{sat}} = N\mu_{\text{eff}}$ which gives a second equation. Then $\mu_{\text{eff}} = 3k_B C / M_{\text{sat}}$. In Fig. 1, we see that $M(T=1.7$ K) tends to saturate at 8 T. Thus M_{sat} is larger than $M(1.7$ K, 8 T) = 0.8 emu/g, from which we deduce a maximum value of μ_{eff} : $8.9\mu_B$, where μ_B is the Bohr magneton. Also, we tried to deduce M_{sat} assuming that $(M_{\text{sat}} - M)$ follows a $1/H$ linear behavior close to the saturation. Using this prediction for systems where spin-glass interactions are present,¹² we find $M_{\text{sat}} = 0.95$ emu/g and therefore $\mu_{\text{eff}} = 7.5\mu_B$. Since we deduce a value of M_{sat} , which is much larger than the maximum

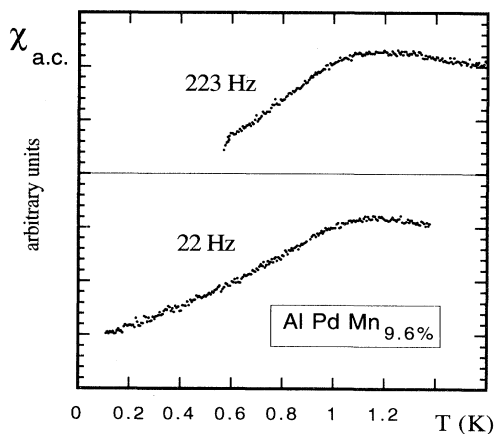


FIG. 3. Temperature dependence of the ac susceptibility measured at two different frequencies of the exciting field of 1 Oe: 22 and 223 Hz.

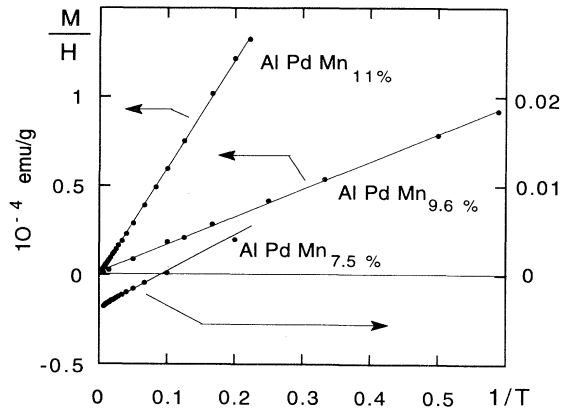


FIG. 4. The dc susceptibility M/H of three Al-Pd-Mn samples (two melt-spun and the single grain) is shown to obey a $1/T$ linear behavior. The value of the applied field is 100 Oe except for Al-Pd-Mn_{7.5%}, where $H = 1$ T. Note the different M/H scale for the latter sample.

magnetization we measure, we do not feel safe about this determination. We will take it as a maximum possible value of M_{sat} . At this step, we have used a classical determination of μ_{eff} : $7.5\mu_B < \mu_{\text{eff}} < 8.9\mu_B$. To obtain a more rigorous estimate of the electronic spin S , we have to discuss the range of temperature where the Curie constant is measured. Our data are obtained well above the temperature T_m of the maximum of susceptibility, i.e., well above the spin-glass transition temperature. Close to T_m , strong correlations exist between the spins and the Curie constant cannot be expressed in terms of a quantum model involving single spins: One can assume that C is proportional to S^2 rather than $S(S+1)$. At $T \gg T_m$, i.e., in a regime of independent spins, we have to use the quantum calculation where $C = Ng^2 S(S+1)\mu_B^2 / 3k_B$ and $M = NgS\mu_B$. Using the latter expressions, we find $2.75 < S < 3.4$ if we take $g = 2$. Also, we have tried to analyze our data in terms of a Brillouin function at a temperature at which we can assume that the spins are independent. This imposes analysis of the data obtained well above T_m , practically above $4T_m$, where magnetic correlations are known to survive in spin glasses. But a reliable fit cannot be obtained at too large a temperature where the magnetization is roughly H linear in our field range. So we choose to use our data obtained at 10 K. The best fit is obtained for $S = 3.3$ and yields a saturated magnetization equal to 0.79 emu/g: See the full line in Fig. 2. We note that the fit gives a spin value larger than $5/2$ and that the data do not lie exactly on the curve given by the best fit. This curve crosses the real M vs H variation two times (see Fig. 2). We cannot exclude the fact that pairs or triplets of strongly correlated near-neighbor Mn atoms survive even at $9T_m$. Thus, it is possible that, at 10 K, we actually measure a mean value of the moments of single Mn atoms, of pairs and of triplets. To check this point, we show our data in a M -vs- H/T diagram in Fig. 5. For a paramagnet, all the points should

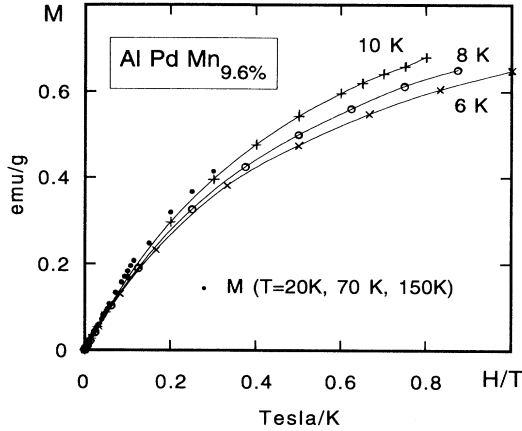


FIG. 5. The magnetization of the Al-Pd-Mn_{9.6%} platelet is shown to disagree with the paramagnetic law: $M = f(H/T)$ at $T \leq 10$ K. The solid circles represent the magnetization measured at 20, 70, and 150 K.

lie on a single curve. We see in Fig. 5 that it is not the case and that, even at 10 K, the data do not follow the behavior of the high-temperature results. The disagreement with a universal law increases when the temperature is lowered, which is typical of the approach to a spin-glass transition (see Fig. 3 of Ref. 13). Once we have roughly estimated the value of S , we calculate the number N of magnetic Mn atoms. We find N to be between 1×10^{-3} and 1.35×10^{-3} of the total number of atoms, i.e., between 1 and 1.4 % of the number of Mn atoms.

The conclusion of this section is the following: Only a few Mn atoms appear to be magnetic from magnetization data analysis. They carry a large spin. Finally we can assume that they interact magnetically to give a spin-glass transition.

III. SPECIFIC-HEAT MEASUREMENTS

In the T range of measurements (Fig. 6), the specific heat C_p is dominated by a broad bump centered around 1 K which, because of its evident similarity with the previous data of the Al-Mn-(Si) series,^{5,11} we identify to a spin-glass ordering. Indeed the temperature of the maximum of C_m/T (C_m being the magnetic specific heat) agrees within 30% with that of maximum of χ_{ac} , as already observed for a -Al_{82.7}Mn_{17.3} and i -Al₈₆Mn₁₄, which are the two phases with the closest values of T_m in this series.

By comparison to the previous series, one can expect that the tail of C_m vanishes around 6 K: above 6 K, C_p reduces to the electronic and lattice contributions. We tentatively describe C_p by a usual $\gamma T + \beta T^3$ law above 5.7 K; because of the small T range available, the corresponding numerical values of γ and β are only indicative, with γ less than 0.5 mJ/mol K² ($\gamma \approx 0.25$ mJ/mol K² is a possible mean value) and $\beta \approx 0.13$ mJ/mol K⁴. Possible additional lattice terms like δT^5 can be present in this T range, which indicate large deviations from an exact De-

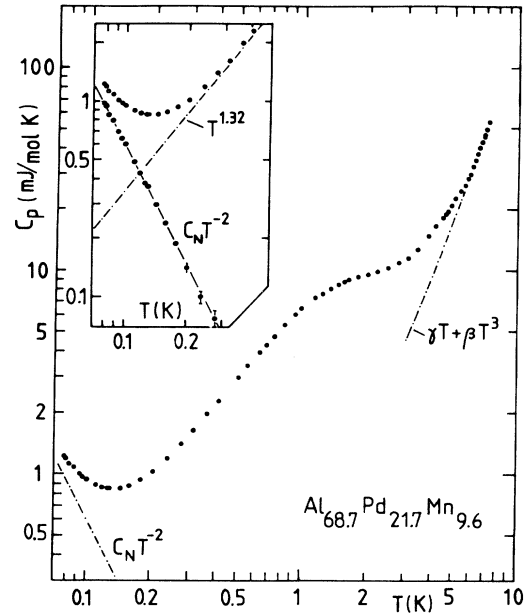


FIG. 6. Specific-heat data of i -Al_{68.7}Pd_{21.7}Mn_{9.6} in a log-log diagram. The dashed line above 3 K represents a possible estimation of the electronic and lattice contributions. The dashed line below 0.2 K is the nuclear hyperfine magnetic contribution deduced from the analysis shown in the inset: below 0.5 K, $C_p = C_N T^{-2} + B T^{1.32}$, when the second term is the magnetic (electronic) contribution.

bye behavior, as in the case of Al-Cu-Fe alloys.¹⁴ So no estimations of a Debye temperature can be done from β .

In the T range below 0.6 K, well below the freezing temperature, where the electronic and lattice contributions become negligible, C_p is very well analyzed as the sum of the magnetic (electronic spins) contribution $C_m(T)$ plus a hyperfine nuclear term $C_N T^{-2}$ (see the inset of Fig. 6):

$$C_p = C_N T^{-2} + C_m(T),$$

where $C_m = B T^n$, with $n = 1.32$ and $B = 7.2$ mJ/mol K^{2.32}. Similar analyses and similar temperature dependence of C_m , slightly more rapid than linear ($1.2 \leq n \leq 1.4$), have already been obtained below T_m in different samples of the Al-Mn series: i -Al₇₅Mn₂₀Si₅,¹¹ a -Al_{82.7}Mn_{17.3},⁵ and decagonal phases T -Al₈₀Mn₂₀ and T -Al₇₈Mn₂₂.⁶ In addition, the prefactor B remains almost independent of the concentration N of really magnetic Mn atoms in the series: B varies at maximum by a factor of 2, whereas the concentration N varies by two orders of magnitude. This universality of $C_m(T)$ observed in metallic spin-glasses, is the signature of long-range RKKY interactions between the spins. The hyperfine nuclear term C_N results from the interaction at the nucleus of the magnetic Mn atoms between the nuclear magnetic spin- I and the effective magnetic field H_{eff} induced by the electronic magnetization (spin- S) of the same atom. There-

fore, C_N is directly proportional to the number N' of moments close to the saturation value,

$$C_N \sim N' |H_{\text{eff}}|^2 \sim N' \langle S \rangle^2.$$

As we did in the case of the metastable Al-Mn series, we assume that the ratio H_{eff}/S does not depend very much on the atomic environment of the magnetic Mn atom and has the same value as in canonical spin glasses like Cu-Mn and Ag-Mn. Therefore, we take $H_{\text{eff}} \approx 6.7$ T per electronic spin $\frac{1}{2}$. If we pose $S=2$ (or an effective moment $\mu_{\text{eff}} \approx 5\mu_B$ in the Curie constant), we find $H_{\text{eff}} = 27$ T.^{6,15}

From $C_N = (6.1 \pm 0.1) \times 10^{-6}$ J K/mol, we obtain $N' = 1.38 \times 10^{-3}$ of the total number of atoms, which corresponds to a fraction of 1.4% of Mn atoms, which are magnetic, in excellent agreement with the magnetization analysis. N' equals the number of really magnetic Mn's independently of their magnetic interactions. Thus, from our calorimetric and magnetic measurements, we conclude that most of the Mn atoms are really nonmagnetic and that the few Mn atoms that are magnetic carry a large spin. Also the specific-heat data confirm the existence of RKKY interactions.

IV. RKKY COUPLING

An important and unexpected result of our magnetic study of the metastable Al-Mn series^{6,15} was that all the (*a*), (*i*), and (*T*) phases obey a universal scaling relation between T_m and the nuclear specific-heat coefficient $C_N \sim NS^2$. Here T_m is the temperature of the maximum of χ_{ac} measured at low frequency. Since T_m varies very little with the frequency, one can use the value of T_m obtained by measurements performed in a relatively large frequency range, say 10–100 Hz. We attributed the relation $T_m \sim (C_N)^a$ to RKKY magnetic interactions between the magnetic Mn atoms. Indeed in the case of spin-glass ordering, T_m is close to the transition temperature $T_c = \langle J \rangle$. When interactions J_{ij} between spins at sites *i* and *j* depend on the distance following a $1/r^3$ law: $J_{ij} = V_0 S(S+1)/r_{ij}^3$, the mean value $\langle J \rangle$ of the interaction energy is proportional to the number N of spins per unit volume. It is the case of RKKY systems, where $T_m \sim NS(S+1)$. Such a quasilinear relation $T_m \sim T_0 x^a$ was early established for canonical metallic RKKY spin-glasses like $\text{Cu}_{1-x}\text{-Mn}_x$ and $\text{Au}_{1-x}\text{-Mn}_x$ (with $a \approx 0.7$) where all the Mn's are magnetic. For $\text{Cu}_{1-x}\text{-Mn}_x$, all the data found in the literature¹⁶ lie on a straight line of slope 0.7 in a $\log T_m$ vs. $\log x$ diagram. As C_N equals $1.2 \cdot 10^{-4}$ J K/mole per at. % of Mn in CuMn,¹⁷ we choose here to represent the same data in a $\log T_m$ -vs- $\log(C_N = x \cdot 1.2 \cdot 10^{-4})$ diagram: See Fig. 7. This will permit us to compare the data of QC's containing Mn atoms with those of crystalline CuMn in the same diagram. The data of AgMn and AuMn lie on a parallel but different straight line, located below that of Fig. 7, since $T_m = 5$ K for AgMn_{1%} and AuMn_{1%} instead of 10 K for CuMn_{1%}.¹⁶ This indicates a different value of V_0 in CuMn and AgMn and, hence, a different electronic density of states in the two systems. As is shown in Ref. 6, in the case of metastable Al-Mn, the scaling relation is also

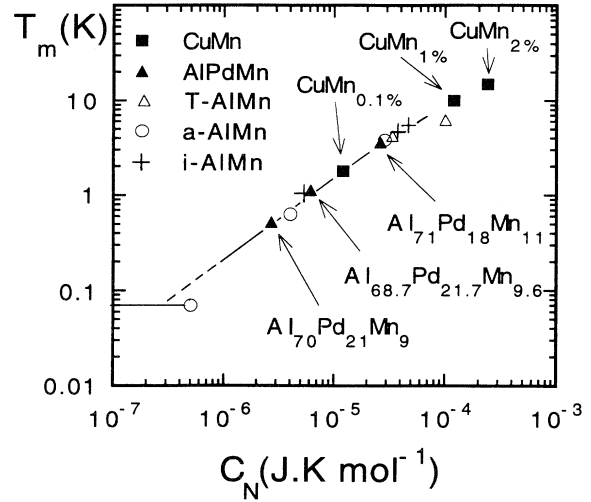


FIG. 7. Freezing temperature as measured by χ_{ac} at a frequency of 115 Hz or less vs the amplitude of the nuclear hyperfine term C_N of the specific heat for all amorphous and quasicrystalline phases of Al-Mn-(Si) and Al-Pd-Mn alloys. C_N is estimated from the Curie constant for Al-Pd-Mn₁₁ (see text). The continuous line was previously established for the metastable Al-Mn-(Si) series (Refs. 6 and 15). Data of Al-Pd-Mn are from this work, except that of Al₇₀Pd₂₁Mn₉ given in Ref. 19. The data of CuMn are also reported on the figure.

obeyed on condition that we use the number of really magnetic Mn atoms, i.e., C_N , instead of the chemical Mn concentration. In the log-log diagram of Fig. 7, all the data are aligned on a *unique* straight line independently of the phase (*a*), (*i*), or (*T*). It is surprising that the scaling relation is unique, which indicates that T_0 and, hence, the potential V_0 of the RKKY interaction is the *same* for all metastable Al-Mn QC's and amorphous phases. A new surprise comes from the fact that the same relation, implying the same value of V_0 , is exactly verified in the present Al-Pd-Mn sample (Fig. 7). It extends the universality of V_0 to the thermodynamically stable QC of perfect structural quality. In addition, this is a strong argument in favor of an *intrinsic* origin of magnetism in the metastable Al-Mn phases. This intrinsic origin was also the conclusion of a NMR study of several Al-Pd-Mn melt spun samples in the composition range between 7.5 and 9.5 at. %.¹⁸

In Fig. 7, we have also reported data obtained by various authors on stable Al-Pd-Mn QC's of other composition (9 and 11 at. % of Mn). Once more, all of these data lie on the same straight line.

The Al₇₀Pd₂₁Mn₉ sample was studied by Chernikov *et al.*,¹⁹ who recently performed a complete magnetic study including specific-heat measurements. The authors used the same analysis of the low-*T* specific heat: They obtained, for $T < 0.25$ K, a magnetic contribution $C_m(T) = 7.6T^{1.38}$ (mJ/mol K) very similar to the present one, and C_N and T_m (from χ_{ac}) values about two times smaller: 2.7×10^{-6} J K/mol and ~ 0.52 K, respectively

(measured at $f = 82$ Hz). We note that the less magnetic character of this sample, by a factor of 2, for a Mn composition of 9 at. % in comparison of 9.6 at. % in our case is compatible with the strong sensitivity of the magnetic character upon the Mn concentration of the Al-Pd-Mn system: See below and Ref. 10. In addition, despite the difference by a factor of 2 in the concentration of moments, we outline that the low- T magnetic contribution $C_m(T)$ is almost similar in both Al-Pd-Mn samples. This confirms the quasi-independence of C_m upon the actual concentration of moments.

From our study on a melt spun $\text{Al}_{71}\text{Pd}_{18}\text{Mn}_{11}$ sample, we have only T_m and the Curie constant C . We can reasonably assume that one can use indifferently C_N or C by using a constant value of C/C_N for all the samples. Indeed, up to now, we found a good agreement between the values of NS^2 given by C_N and C for the previous samples. For our single grain we found $C/C_N = 1.2 \times 10^3$ emu/JK. We deduce that C_N should equal 2.4×10^{-5} JK/mol for $\text{Al}_{71}\text{Pd}_{18}\text{Mn}_{11}$. For this sample, T_m is given by a dc magnetization measurement: The sample is zero field cooled, and a field of 8.6 Oe is applied at 2 K (see Fig. 8). Subsequently, the temperature is increased: the magnetization exhibits a maximum at $T_m = 3.6$ K. For spin glasses, this procedure gives a value of T_m only a few percent smaller than that obtained from ac susceptibility. As is shown in Fig. 8, when the temperature is decreased from high temperatures, the field-cooled magnetization is flat; more exactly it decreases slightly below T_m , which is typical of spin glasses.

Another surprise comes from comparison of the value of V_0 of QC's containing Mn and that of crystalline CuMn . The value of V_0 is known to be the largest for CuMn in the series of dilute alloys with Mn (AuMn , AgMn , etc.). In Fig. 7, we observe that the CuMn and QC's data lie on the same curve. This implies the same value of V_0 although one should expect very different values due to the expected different electronic densities of states of these systems, especially at the Fermi level.

We conclude from this section that the spins of the

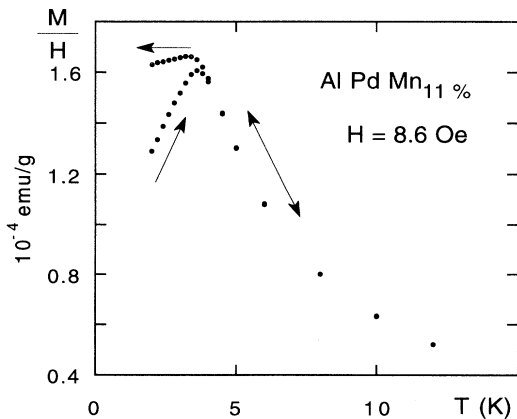


FIG. 8. Temperature dependence of the zero-field-cooled and field-cooled magnetization of Al-Pd-Mn_{11%} in a field of 8.6 Oe.

really magnetic Mn atoms are coupled by RKKY interactions involving an energy interaction V_0 , which does not depend on the phase, metastable (i)-, (a)-, or (T)-Al-Mn or stable Al-Pd-Mn. This conclusion also supports an intrinsic origin of magnetism in the metastable phases. Also we note that V_0 is as large as in crystalline CuMn .

V. GENERALITY OF MAGNETISM OF QC'S CONTAINING Mn

Here we discuss the very general behavior of QC's containing Mn atoms. First we have found that, as in metastable Al-Mn compounds, a few Mn atoms are really magnetic.

In the latter section, we have shown that the few Mn atoms that are magnetic are coupled by RKKY interactions. We have found that the interaction energy V_0 does not depend on the phase [metastable or stable (a), (i), or (T)] and on the preparation (melt-spun ribbons or single grain). This suggests that the part of the electronic density of states that is involved in V_0 is similar in all the studied phases and surprisingly similar to that of CuMn .

Now we point out that the magnetism of the QC's containing Mn atoms is intrinsic. This could be deduced from the early studies on metastable Al-Mn phases from which one can conclude a random distribution of magnetic Mn atoms in the samples. For instance, a complete study of the nonlinear susceptibilities of i -Al-Mn-(Si) showed the existence of a three-dimensional spin-glass transition.⁴ The data were easily interpreted in terms of a monotonic increase of correlation volumes V_c when the temperature is decreased down to the transition temperature T_c : $V_c \sim (1 - T/T_c)^{-d\nu}$. In addition, the correlations were found to spread over very large distances: At $1.1T_c$, a correlation volume V_c contains 2×10^5 spins. These results discard the fact that magnetic Mn atoms are located in intergrain regions or in small parasitic phases. Also we note that the number of magnetic Mn atoms increases drastically but always monotonically when the chemical Mn concentration x is increased: See Figs. 4 and 7. This is true whatever the preparation technique is. In Fig. 4, we represent the temperature dependence of the susceptibility of our platelet and of the two melt-spun samples: $\text{Al}_{70.5}\text{Pd}_{22}\text{Mn}_{7.5}$ and $\text{Al}_{71}\text{Pd}_{18}\text{Mn}_{11}$ denoted, 7.5 Mn and 11 Mn, respectively. The applied field for the 11 Mn equals 10 Oe. Due to the very small magnetism of the 7.5 Mn, a field $H = 1$ T was applied to provide a measurable signal. But because of this large value of the field, the susceptibility equals M/H only for $\mu_{\text{eff}}H \ll kT$, i.e., at $T \gg 4$ K. We find the following values of the Curie constant: C (11 Mn) = 6.44×10^{-4} emu/g (i.e., 2.86×10^{-2} emu/mol), C (9.6 Mn) = 1.6×10^{-4} emu/g (i.e., 7.5×10^{-3} emu/mol), and C (7.5 Mn) $\approx 3 \times 10^{-6}$ emu/g (i.e., 1.39×10^{-4} emu/mol). We observe that the Curie constant C varies monotonously with the Mn concentration. Now we can estimate the ratio of the Curie constant C due to the really magnetic Mn atoms to the Curie constant $C_{\text{calc}} \sim N_T \mu^2 = N_T S(S+1) (g\mu_B)^2$, which should be that of the system if all the Mn atoms were magnetic and carried a spin $S = 2.5$. We find C_{calc} equal to 0.48, 0.42, and

0.33 emu/mol for the (11 Mn), (9.6 Mn), and (7.5 Mn), respectively. In Fig. 9, we have plotted the ratio of the measured Curie constant to C_{calc} , i.e., the value of $(N\mu_{\text{eff}}^2)/(N_T\mu^2)$ vs the nominal chemical Mn concentration x in a semilog diagram. The data obtained for Al-Pd-Mn QC's, melt spun or single grain, lie on a single curve. We have also reported on the same figure the data that can be deduced from a recent study on Al-Pd-Mn single grains²⁰ containing about 8.7 and 9.4 at. % of Mn: The data lie on the previous curve. In the same figure we have also represented the data for metastable Al-Mn systems: they also lie on a single curve, independently of the phase (a), (i), or (T). It means that the Curie constant due to the really magnetic Mn atoms of Al-Mn systems does not depend drastically on the method of preparation and of the phase. For Al-Mn systems, $N\mu_{\text{eff}}^2$ is deduced from the nuclear term C_N of the specific heat,^{6,15} when H_{eff} is assumed to equal 6.7 T per electronic spin $\frac{1}{2}$ (see Sec. III).

Very surprisingly, the Al-Pd-Mn QC's, which are known for the lack of sizable defects, are much more magnetic than the Al-Mn metastable compounds. Indeed, if metastable Al-Mn could exist with only 10% of Mn, we could deduce from the extrapolation of the Al-Mn curve of Fig. 9 that it should be four orders of magnitude less magnetic than Al-Pd-Mn_{10%}. We note that the rapid increase of C/C_{calc} with x explains why a very small chemical concentration gradient of Mn leads to a large magnetization variation. For instance, the Curie constant of a sample of Al-Pd-Mn containing 9.25% of Mn is twice smaller than that of a sample containing 9.6% of Mn (see Fig. 9). In our case, we can suppose a constant gradient of the Mn concentration along the $A2$ axis of our grain. Since the mean value of the magnetization of the grain is half of that of the platelet, it is easy to calculate that the grain should contain 9.1% of Mn at one end and 9.6% of Mn at the other end, where we have cut the platelet.

At this step we can conclude the universality of the magnetism of the QC's containing Mn atoms. But a question arises about the low-temperature specific heat. The electronic term γ of our QC grain is about $\frac{1}{4}$ of that of pure Al. This indicates that the electronic density of states at the Fermi level is very small, as is the case in grains of Al-Cu-Fe (Ref. 21) and as was confirmed by XPS measurements.²² So we discard the assumption of an enhanced density of states at the Fermi level due to a virtual bound state. Thus the lack of magnetism of most Mn atoms cannot be explained by a Kondo-like effect. In turn, this poses new questions: Why the linear T term of the specific heat of metastable QC's (Refs. 5 and 6) is 20–30 times larger than that of our grain? Is this elec-

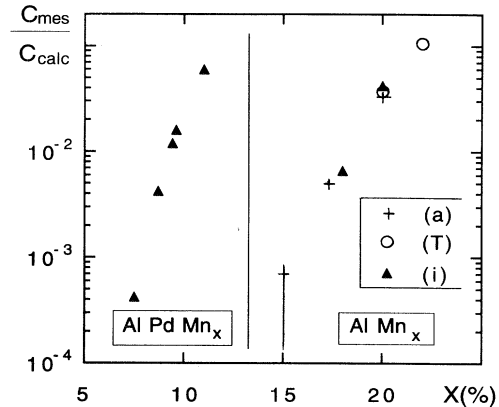


FIG. 9. In Al-Pd-Mn QC's as well as in Al-Mn metastable compounds, the ratio (C/C_{calc}) is shown to increase drastically and monotonically when the Mn chemical concentration increases. C is of the Curie constant due to the really magnetic Mn atoms and C_{calc} is the calculated when it is assumed that all the Mn atoms magnetic and carry a spin equal to 2.5. The perfect Al-Pd-Mn QC's are surprisingly more magnetic than the Al-Mn systems.

tronic term very sensitive to the method of preparation, or is it from another origin than purely electronic?

CONCLUSION

In summary, from our magnetization, magnetic susceptibility and specific-heat measurements in a single QC grain Al-Pd-Mn, we conclude the overall similarity of the magnetic properties of thermodynamically stable Al-Pd-Mn QC's to the metastable Al-Mn-(Si) series. All are characterized by a feeble fraction of Mn magnetic sites with a rather large spin value, long-range RKKY interactions resulting in a spin-glass-state ordering at a few degrees kelvin. The universality of these properties enables us to conclude the intrinsic origin of the Mn magnetism in the metastable phases, an assumption that was still recently a matter of debate. An unexpected and unexplained result is the similarity of the strength of RKKY interactions among amorphous, quasicrystalline and even a dilute crystalline alloy such as CuMn , which is known to exhibit a large RKKY potential.

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