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Experimental evidence for the existence of enhanced density of states and canonical spin-glass behavior in Al-Mn (-Si) quasicrystals

C. Berger, J. C. Lasjaunias, J. L. Tholence, D. Pavuna,* and P. Germi
Centre National de la Recherche Scientifique, Boîte Postale 166 X, 38042 Grenoble Cédex, France

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We report experimental evidence for an enhanced density of states at the Fermi level in $Al_{86}Mn_{14}$ and $Al_{75}Mn_{20}Si_5$ quasicrystals (QC) as indicated by the low-temperature specific heat and resistivity. The excess specific-heat term $\Delta\gamma$ is proportional to the Mn concentration in these QC samples as is the case for dilute *Al*Mn alloys. Spin-glass-like behavior is observed in both QC samples. In Al-Mn-Si, the relative frequency dependence of the ac susceptibility cusp is comparable to canonical spin glasses such as *Ag*Mn or *Cu*Mn.

Ever since the discovery of quasicrystals (QC) the interpretation of their magnetic[1,2] or electronic[3] properties has been fairly controversial. In a previous study Berger and co-workers[3] have proposed that the high measured resistivity (150–200 $\mu\Omega$ cm) of Al-Mn QC could be interpreted within the framework of a Friedel-Anderson *s-d* model which was originally developed for dilute Al 3*d* alloys. Although in a somewhat different context, other authors[4,5] also proposed that the density of states (DOS) at E_F should be enhanced. However, to our knowledge, no experimental evidence[6,7] for the enhanced DOS has been reported prior to this paper.

In this paper we present the very-low-temperature specific heat (C_p) and frequency variation of the ac magnetic susceptibility (χ_{ac}) on QC and recrystallized (C) samples of $Al_{86}Mn_{14}$ and $Al_{75}Mn_{20}Si_5$. Our main results are that the excess specific-heat term $\Delta\gamma$ (due to Mn) is proportional to the Mn concentration in these QC samples as in the well-known case for dilute *Al*Mn alloys. Spin-glass-like behavior is observed in both QC samples. In Al-Mn-Si, the relative frequency dependence of the ac susceptibility cusp is comparable to canonical spin glasses such as *Ag*Mn or *Cu*Mn.

All samples were prepared by melt spinning in widths of up to 6 mm with average thickness ~20 μm. They were characterized in great detail by x-ray diffraction and transmission electron microscopy. $Al_{75}Mn_{20}Si_5$ consists almost entirely of the QC phase, with a typical grain size ~0.5 μm and with less than about 10 vol% of fcc Al. $Al_{86}Mn_{14}$ consists of ~70 vol% of QC phase with typical grain size ~1 μm. The remaining represents fcc Al which contains up to 3 at.% Mn in solid solution. Because of this second phase, we have also produced and studied the behavior of Al–3 at.% Mn alloy.

Specific-heat measurements were performed on a dilution refrigerator by means of a step-by-step transient heat-pulse technique;[8] the ac susceptibility and magnetization were measured simultaneously down to 40 mK in a small dilution insert.[9]

As shown in Fig. 1, linear specific-heat variation ascribed to the electronic contribution can be observed in all samples, but at very low temperatures ($\leq$ 0.3 K). For recrystallized $Al_{86}Mn_{14}$ (annealed at 600 °C) a γ value of 1.35 mJ/molK^2 is found, in excellent agreement with values reported for orthorhombic Al_6Mn (Ref. 10) and Al in the normal state; both of which are present in our sample.[11] In QC samples, the amplitude of this electronic term is estimated by taking into account the hyperfine contribution ($\propto T^{-2}$) which increases rapidly at lower temperatures. For QC $Al_{86}Mn_{14}$, the analysis with a γT term between 0.08 and 0.25 K leads to $\gamma = 10 \pm 0.5$

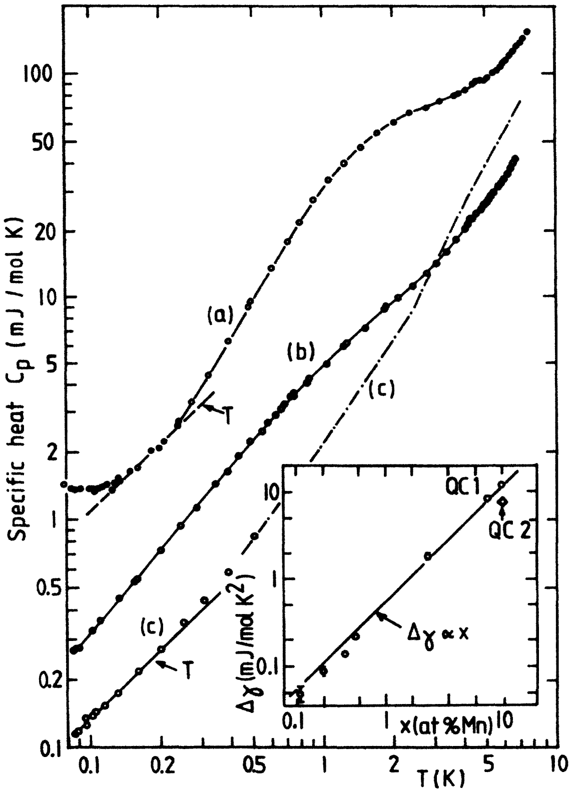

FIG. 1. Specific heat of (a) $Al_{86}Mn_{14}$ QC, (b) Al–3 at.% Mn solid solution, and (c) $Al_{86}Mn_{14}$ recrystallized. In the inset, the electronic term in excess to γ of pure Al vs the Mn concentration in the range from dilute solid solution up to the QC phases Al-Mn (QC 1) and Al-Mn-Si (QC 2).

mJ/mol K^2. In the inset of Fig. 1 we plot the amplitude $\Delta\gamma$ of this low-temperature electronic term in excess to the γ value of pure Al. We emphasize that $\Delta\gamma$ scales with the overall percentage of the Mn-*s* in the sample, in good agreement with earlier results for very dilute $Al\mathrm{Mn}_x$ ($x \leq 0.45$ at.%) alloys[12] and our own measurements on $x = 3\%$. We have already measured and reported the same proportionality with concentration of the residual resistivity[3] ($\rho_{4.2\,\mathrm{K}} = 25$, 70, and 100 $\mu\Omega$ cm for samples containing 3, 10, and 14 at.% Mn, respectively). Taking into account the correction for about 30 vol% of Al-3 at.% Mn in the $\mathrm{Al_{86}Mn_{14}}$ sample, we estimate that γ for a $\mathrm{Al_{80}Mn_{20}}$ QC would be ~ 13 mJ/mol K^2.

In the Al-3 at.% Mn sample, above the quasilinear regime (with $\gamma = 3$-3.3 mJ/mol K^2) the slight departure ΔC from a $\gamma T + \beta T^3$ law around 1 K is ascribed to the onset of magnetic interactions.[13] It becomes a broad bump in $\mathrm{Al_{86}Mn_{14}}$ QC, somewhat similar to other C_p data[6] on $\mathrm{Al_{80}Mn_{20}}$ QC, with a maximum amplitude for $\Delta C/T$ at 1.4 K (ΔC being defined as the excess above the $\gamma T + \beta T^3$ law, with $\gamma = 10$ mJ/mol K^2). This bump does not exist in a fully crystallized sample.[11] In χ_{ac} a rounded maximum also appears at 1.0 K (see Table I). We thus ascribe the C_p anomaly to magnetic interactions, since the relative positions of the C_p and χ maxima are in agreement with data on spin glasses.[14] We have calculated the entropy S_m by integrating $\Delta C/T$ between 0 and 7 K. Estimating the phonon term from the data above 5 K, which corresponds to a Debye-temperature range of 230–300 K, we find $S_m = 60$ to 70 mJ/mol K.

For $\mathrm{Al_{75}Mn_{20}Si_5}$ QC, the broad C_p maximum is shifted to higher temperatures ($T > 10$ K),[15] and the C_p variation between 0.3 and 7 K is well described by a power $T^{1.2}$ law (Fig. 2); the amplitude of this term ascribed mainly to an electronic contribution allows us to estimate $\gamma \sim 9 \pm 1$ mJ/mol K^2, which is therefore smaller than the estimated value for $\mathrm{Al_{80}Mn_{20}}$ QC phase (≈ 13 mJ/mol K^2). Furthermore, the nuclear hyperfine contribution, $C_N = AT^{-2}$ with $A = 3.75 \times 10^{-5}$ J K/mol (see inset of Fig. 2) is ten times larger than in $\mathrm{Al_{86}Mn_{14}}$ QC. Since this amplitude cannot be of electric quadrupolar origin [on the basis of the quadrupolar splitting energies obtained from NMR (Ref. 16) or Mössbauer[17] data], we ascribe it to the hyperfine field on the nuclei of magnetic Mn *s* sites. In that case, A is directly related to the concentration of localized moments close to the saturation[18] in both QC samples, and can give similar information as high-field saturation magnetization.

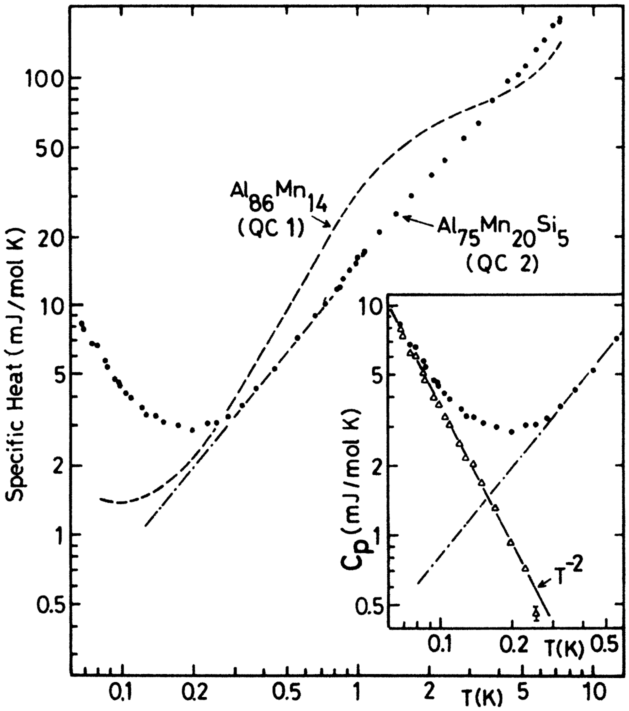

FIG. 2. Specific heat of $\mathrm{Al_{75}Mn_{20}Si_5}$ compared to $\mathrm{Al_{86}Mn_{14}}$ (dashed curve). In the inset, C_p is analyzed as the sum of the electronic term, extrapolated from data above 0.3 K, and an hyperfine nuclear T^{-2} contribution.

Therefore, both modification of the magnetic bump and the hyperfine nuclear term indicate an enhanced magnetic character in Al-Mn-Si as compared to AlMn. We now discuss the magnetic measurements which confirm this point.

The magnetization of $\mathrm{Al_{86}Mn_{14}}$ is proportional to the field down to the lowest temperature and up to 3000 Oe. At that field it attains only $\frac{1}{400}$ of the saturation expected for 14% of free Mn spins with assumed $S = 1$ (see Table I). The field-cooled magnetization (3000 Oe) increases slowly when the temperature decreases, without marked anomaly around 1.0 K. The thermoremanent magnetization tends to 1.5×10^{-2} emu/g at 80 mK; it decreases exponentially when T increases[19] and disappears around T_f as in a spin glass.

The ac susceptibility was measured in a peak-to-peak ac field of 2 Oe at 113 Hz. It goes through a rounded maximum around $T_f = 1.0$ K. All these characteristics, small magnetization, susceptibility maximum, and remanent

TABLE I. Magnetic parameters deduced from the ac susceptibility analyzed as $\chi = \chi_0 + C/(T + \Theta)$, for $5 < T < 150$ K, and electronic C_p term γ. x denotes the concentration of magnetic Mn.

	T_f (K)	C (10^{-4} emu/g)	Θ (K)	χ_0 (10^{-6} emu/g)	μ_{eff} (μ_B)	$10^3 x$ $S = 1$	$S = 2$	γ mJ/mol K^2
$\mathrm{Al_{86}Mn_{14}}$ QC	1.0	1.5 ± 0.05	0	4 ± 0.1	0.5 ± 0.05	4.5 ± 0.5	1.5 ± 0.2	10 ± 0.5
$\mathrm{Al_{86}Mn_{14}}$ recrystalized		0.15 ± 0.05	0	1 ± 0.2	0.2 ± 0.05	0.45 ± 0.1	0.15 ± 0.04	1.35 ± 0.05
$\mathrm{Al_{75}Mn_{20}Si_5}$ QC	4.7	13 ± 2	4	35 ± 5	1.3 ± 0.1	43 ± 6	15 ± 2	9 ± 1
$\mathrm{Al_{75}Mn_{20}Si_5}$ recrystalized		0.25 ± 0.05	0	10 ± 1	0.2 ± 0.05	0.8 ± 0.2	0.25 ± 0.05	

magnetization, suggest a spin-glass behavior below 1 K. However, only the study of the divergence of the nonlinear magnetization terms or of the frequency dependence of T_f can be considered as a definitive proof of the existence of the spin-glass transition. As to the rounded form of the maximum in χ_{ac} it could be due to (i) concentration fluctuations or (ii) freezing of magnetic clusters (as an alternative to spin-glass transition). After recrystallization, χ_{ac} decreases to smaller values (see Table I) in good agreement with earlier work[1] and in accordance with the specific heat.

For the frequency dependence of χ_{ac} in $Al_{75}Mn_{20}Si_5$, we observed a much sharper cusp at $T_f \approx 4.8$ K at low frequency (Fig. 3). The important result is that the cusp temperature T_f varies slowly with frequency. This relative variation of T_f can be measured as $\Delta T_f/(T_f \Delta \log_{10} f)$, where ΔT_f is the variation of T_f associated with the logarithm of the varying frequency, $\Delta \log_{10} f$. Its value is ≤ 0.015, very close to the small values published for canonical spin glasses such as *Au*Fe (0.01), *Cu*Mn (0.007), or *Ag*Mn (0.005).[19] This frequency variation of χ_{ac} therefore clearly indicates a spin-glass behavior in this sample.

High-temperature susceptibilities of all the samples have been analyzed in terms of a Curie-Weiss-like susceptibility, $C/(T+\Theta)$ plus a constant contribution χ_0 (Fig. 4). Table I contains the magnetic data of QC and *C* samples. The best fits are obtained with $\Theta = 0$ for $Al_{86}Mn_{14}$ QC and $\Theta \cong 4$ K for $Al_{75}Mn_{20}Si_5$ QC. The spin value of magnetic atoms is not well determined and, due to the high Kondo temperature (600 K), it is possible that only groups of more than ~4 Mn are magnetic.[13] A close comparison with the magnetic behavior of *Cu*Mn spin glass gives an average *S* value $1 \lesssim S \lesssim 2$ per Mn atom.[20] We have deduced the molar concentration *x* from *C*, using these two *S* limiting values, in Table I. For $Al_{86}Mn_{14}$ QC the concentrations *x* are of the same order as those obtained from the magnetic entropy $S_m = xNk_B \ln(2S+1)$ which gives $x = 7(\pm 0.7) \times 10^{-3}$ or $4.6(\pm 0.5) \times 10^{-3}$ [i.e., $5(\pm 0.5)\%$ or $3.3(\pm 0.3)\%$ of the Mn atoms] taking, respectively, $S = 1$ or $S = 2$. For Al-Mn-Si, the effective magnetic field (200 ± 20 kOe) deduced from the nuclear C_p term and assuming $S = 2$ would be in good agreement with the value measured in spin glasses such as *Cu*Mn (280 ± 10 kOe).[21] Our estimates of the average effective magnetic moment per Mn, $\mu_{eff} = 0.51$ and $1.3\mu_B$ for $Al_{86}Mn_{14}$ and $Al_{75}Mn_{20}Si_5$, respectively, are in excellent agreement with previously reported results.[1,2] Finally, the difference in the magnetic characteristics of $Al_{86}Mn_{14}$ and $Al_{75}Mn_{20}Si_5$ QC samples is confirmed by low-temperature magnetoresistance measurements.[22]

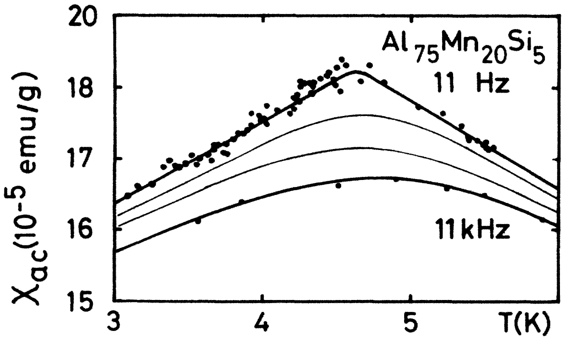

FIG. 3. Frequency dependence of ac susceptibility of $Al_{75}Mn_{20}Si_5$ QC, at 11, 111, and 1100 Hz, and 11 kHz.

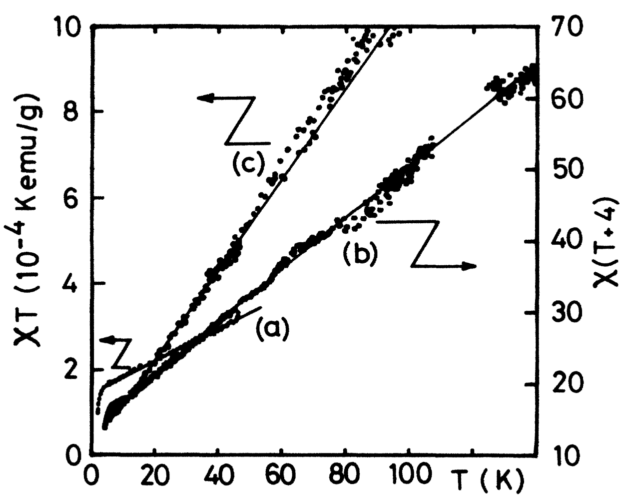

FIG. 4. χT, or $\chi(T+\Theta)$, as a function of temperature for (a) $Al_{86}Mn_{14}$ QC, (b) $Al_{75}Mn_{20}Si_5$ as-quenched (QC), and (c) $Al_{75}Mn_{20}Si_5$ recrystallized (β phase).

Simple interpretation of our results can read as follows. The fact that electrical resistivity ρ_0 and excess linear specific-heat term $\Delta\gamma$ are proportional to the Mn concentration in all our QC samples suggests that as a crude approximation we can consider Mn atoms as "isolated impurities" in an Al matrix. The Mn *d* states hybridized with Al *s,p* states then give rise to an enhanced DOS at E_F. The magnitude of electrical resistivity is obtained by assuming the *s-d* scattering process[3] in which each Mn contributes ~8 $\mu\Omega$ cm/at.% Mn in a direct analogy with a well-known Friedel-Anderson *s-d* model for dilute alloys.

Clearly, the actual physical picture is more complex due to the differing magnetic state of $\lesssim 10\%$ of all Mn sites in QC samples. These magnetic sites result in an observed Curie-Weiss-like susceptibility term and spin-glass behavior at low temperatures. The spin-glass "order" is apparent in the maximum of the specific-heat curve, in the ac susceptibility cusp, and also in the hyperfine term of the specific heat. On the contrary, in fully recrystallized samples all Mn atoms are nonmagnetic and there is no evidence for enhanced DOS (or $\Delta\gamma$ proportional to the Mn concentration in specific heat) in that case.

In conclusion, the magnetic behavior of $Al_{86}Mn_{14}$ and $Al_{75}Mn_{20}Si_5$ quasicrystals indicate spin-glass-like freezing. Moreover, the relative frequency dependence of ac susceptibility cusp in Al-Mn-Si is found to be comparable to that usually observed in canonical spin-glasses such as *Ag*Mn, *Cu*Mn, and *Au*Fe. The hyperfine nuclear specific-heat term observed at very low temperatures (< 300 mK) is much larger for $Al_{75}Mn_{20}Si_5$ as compared to $Al_{86}Mn_{14}$ which is "less" magnetic. The same trend is observed in the magnetoresistance which is positive in $Al_{86}Mn_{14}$ and becomes negative in $Al_{75}Mn_{20}Si_5$.[22] An excess electronic specific-heat term (compared to pure Al) $\Delta\gamma$ as well as residual resistivity are proportional to the Mn concentration in the QC samples. This we interpret within a simple *s*-*d* model as an indication that the DOS at the Fermi level is somewhat enhanced due to the hybridization of Mn *d* states with *s* states of the Al matrix.

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*Present address: Physics Department, Ecole Polytechnique Fédérale, 1015 Lausanne, Switzerland.

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