Evidence of a Spin-Glass Transition in the Quasicrystal $Al_{73}Mn_{21}Si_6$

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We give a definite answer to the question whether or not the quasicrystal i-$Al_{73}Mn_{21}Si_6$ is a true three-dimensional spin glass by measuring the linear (χ_{ac} and χ_{dc}) and dc nonlinear susceptibilities [$A_3(T),\ldots$]. We show that the magnetic correlations expand over large distances with decreasing T and that $A_3(T)$ diverges following the spin-glass transition scaling law with finite T_c. From A_3 and χ_{dc} we deduce separately and in the $H=0$ field limit the number (1.3% of the Mn concentration) and the moment (large, $7.5\mu_B$) of the magnetic entities, which can be attributed to Mn clusters.

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Three different structural AlMn(Si) phases can exist: amorphous, quasicrystal (QC), and crystalline. For a comparable concentration x of Mn, a crystal is not magnetic, reminiscent of Kondo systems, in contrast with the QC and amorphous phases.[1-4] So which structural arrangements produce differences in the macroscopic magnetic properties between the three phases? Before answering this question, one has to characterize the magnetic states of the amorphous and QC phases. We are dealing with a nontrivial structure, where the electronic mean free path is small (of the order of interatomic distances), and where possibly only a few Mn atoms are magnetic.[5] Therefore one has to answer the following questions. Can correlations between the magnetic Mn exist? Over which spatial scale ξ and over which space dimension d can they expand? Does a transition exist; i.e., does ξ diverge at a critical temperature T_c? In QC and in amorphous phases, the ac susceptibility $\chi_{ac}(\omega=\text{const},T)$ exhibits a cusp[1-4,6] at a temperature T_m, which depends on ω following a Fulcher law,[2] and magnetic hysteresis is present at low temperature.[3,6] This is the reason why the term spin glass (SG) is generally used for these systems. Actually the definition of a SG transition is the divergence of ξ at T_c. But neither a cusp of χ_{ac} nor magnetic hysteresis are probes of the spatial expansion of the magnetic correlations and *a fortiori* of a phase transition: These properties are observed in true SG's as well as in standard superparamagnets where the correlations can exist only within clusters[7] of constant finite size ξ. In the latter case, thermally activated energy barriers for overturning the cluster moments are responsible for the cusp of χ_{ac} and for the hysteresis. Only the measurement of the equilibrium linear (χ_{eq}) and nonlinear (A_3,A_5) susceptibilities of the magnetization M above T_m gives a definite evidence of a transition. The Curie constant C, and A_3 and A_5 are the prefactors of the odd powers of $\mu_B H/kT$ of the series expansion of M and appear in the development of M/H as follows:

$$M/H = C/T - A_3(T)(\mu_B H/kT)^2(1/T) + A_5(T)(\mu_B H/kT)^4(1/T) - \cdots . \quad (1)$$

Here T should be replaced by $T+\theta$ in the case of a Curie-Weiss behavior. If A_3 is T independent, the system is a superparamagnet whereas if A_3 diverges at T_c, it is a spin glass. This point is the first purpose of this paper.

Another unanswered question is what are the values of the number N and of the effective moment p_{eff} of the magnetic Mn in a sample containing N_T Mn atoms? This question follows from the drastic x dependence of Np_{eff}^2 deduced, for instance, from the Curie constant[8,9] $C=Np_{eff}^2/3k$ above T_m or the hyperfine term $C_H=NH_{hyp}^2$ ($H_{hyp}\sim p_{eff}$) of the specific heat.[8] Np_{eff}^2 vanishes below $x=15\%$, increases very rapidly with x, but never reaches the value obtained in various other Mn alloys, i.e., for $N=N_T$ and $p_{eff}\approx 5\mu_B$. To know whether N/N_T or p_{eff} (or both quantities) vary drastically with x, requires a second equation. Theoretically, it is given by the saturated magnetization $M_{sat}=Np_{eff}$. But even very large fields[6] cannot saturate M as is the case for SG. Moreover, field-induced moments on the nonmagnetic Mn can appear in large fields[10] and spoil the result. In this paper, we use the fact that the ratio A_3/C allows us to deduce p_{eff} in the $H=0$ limit. We focus on the study of a QC ($x=21$ at.%) in an attempt to answer the above questions.

To illustrate that C, A_3, and A_5 are powers of ξ, we use the following physical picture for a system of N spins, each of moment p_{eff}. The spins can be correlated by exchange interactions J only within clusters of linear size ξ (given in spacing units). This results in N/n-independent clusters each of n spins ($n=\xi^d$) and of giant moment m. Then n is a measure of the cluster size.

The paramagnet case corresponds to $n=1$. M can be calculated with the standard magnetic parameters:[11,12] $M=(N/n)\langle M\rangle_m$, where $\langle M\rangle_m = m\mu_B L(m\mu_B H/kT)$ per moment $m\mu_B$ of a cluster and $L(X)=X/3-X^3/45+\cdots$ is the Langevin function used in the classical approach for isotropic m directions. One finds $C=\frac{1}{3}\times(m^2/n)N\mu_B^2/k$, $A_3=\frac{1}{15}Cm^2$, and $A_5\sim m^4$. For only $+J$ interactions, $m=np_{\rm eff}$: $C\sim n$ gives the cluster size. For random $+J,-J$ interactions (as in SG's), the variance $\langle m^2\rangle^{1/2}$ of m equals $\sqrt{n}p_{\rm eff}$ leading to the same linear susceptibility ($C=Np_{\rm eff}^2/3k$) as for paramagnets. But $A_{2i+1}(T)\sim\langle m^2\rangle^i\sim n(T)^i$. Then it is $A_3\sim n$ (and not C) which gives the cluster size. The model applies simply to superparamagnets at low T, like, for instance, Fe clusters in alumina:[7] ξ is the T-independent cluster size. Thus n and m are T independent, and C, A_3, and A_5 are also.

In ferromagnets and SG's, the thermal fluctuations split the system in N/n clusters; at decreasing T, $\xi(T)$ and $n(T)$ increase (and diverge at T_c) while N/n decreases. For ferromagnets, $C\sim n$ diverges at T_c. In a SG, $A_3\sim n$ diverges as n at T_c while $\chi_{\rm eq}=C/T$ is not critical. For T_c finite, one has that $\xi(T)\sim t^{-\nu}$, where $t=(T-T_c)/T$. Then $n=n_0t^{-d\nu}$ and $A_{2i+1}\sim t^{-d\nu i}$, which allows us to recover the standard equations:

$$A_3(T)/C=m^2/15=Bt^{-\gamma},\quad A_5\sim t^{-2\gamma-\beta}, \tag{2}$$

with $\gamma=d\nu$, $\beta=0$. At this step the model only fails to account for $\beta\neq 0$. Considering a fractal dimension d^* for the clusters, one corrects the model[12,13] by assuming that $P(n)\sim n^{-1-d/d^*}$ is self-similar up to $n_{\max}(T)=\xi^{d^*}$. This yields $\gamma=(2d^*-d)\nu$, $\beta=(d-d^*)\nu$. Other laws are also predicted for $A_3(T)$ since $\xi(T)$ depends on d/d_c, where d_c is the lower critical dimension: $2<d_c<3$ in SG for local Ising spins.[14] At $d<d_c$ no transition occurs[15] but A_3 varies as $T^{-\Delta}$. At $d=d_c$, $T_c=0$ and[16] $A_3\sim\exp(1/T^2)$. At $d=3$, A_3 and A_5 diverge at $T_c\neq 0$.

At finite T_c, an important result of the complete calculation is the value of B in Eq. (2): $B=Kn_0p_{\rm eff}^2/15$. For identical clusters $K=1$, but in the general case K depends on the distribution of cluster size $P(n)$ over which one integrates $\langle M\rangle_m$. In previous studies we deduced $Kn_0=1\pm 0.1$ for two SG's which differ by the range of the interactions and where $p_{\rm eff}$ is known: a Ruderman-Kittel-Kasuya-Yosida (RKKY) CuMn[11] and an insulating Mn fluorophosphate.[12] In the following, we assume that $Kn_0=1$ also in the present case.

Ribbons (≈ 20 μm thick) of $Al_{73}Mn_{21}Si_6$ were melt spun under He atmosphere. X-ray diffraction shows that the sample consists almost entirely of the icosahedral phase, with no other phases and with less than 5% of residual Al. In the latter no more than 3% of Mn is expected which will not affect the magnetic properties of the sample since Al-3%Mn solid solution is not magnetic.[2,4] Both M and $\chi_{\rm ac}$ are measured by an extraction method in the same custom built magnetometer[11,12] containing 0.22 g of ribbons. Special care is taken to have T stable within a few mK at varying field. Each data point is obtained from a numerically filtered set of fifty extractions. We can detect $M\geq 10^{-7}$ emu with a resolution better than 1 part in 10^4 for $M\geq 10^{-3}$ emu.

Linear ac and dc susceptibilities are plotted as a function of $1/T$ in Fig. 1. $\chi_{\rm ac}(h_{\rm ac}=0.5$ Oe, $\omega=22$ Hz, $T)$ is maximum at $T=5.82\pm 0.05$ K (open circles). $M(T)$ (solid circles) is measured in a dc field $H=365$ Oe. $\chi_{\rm eq}$ (crosses) is deduced from the $M(H)$ analysis (see below). All the data in the 7.5–17-K range and $\chi_{\rm eq}$ down to 6 K can be accurately fitted by $\chi_{\rm eq}=\chi_0+C/T$ (see Fig. 1) with $C=5.30\times 10^{-4}$ emu/g and $\chi_0=1.2\times 10^{-5}$ emu/g. M/H and $\chi_{\rm ac}$ deviate from $\chi_{\rm eq}$ below 7.5 K due, respectively, to the increase of the nonlinear terms of $M(H)$ at decreasing T and to dynamical effects. We attribute the Curie term C/T to the magnetic Mn and χ_0 to the matrix including the Kondo-like Mn. So we will fit $M/H-\chi_0$ by Eq. (1).

Equilibrium nonlinear susceptibilities are obtained from the plot of M/H as a function of $(1/T)(\mu_BH/kT)^2$; see Fig. 2. The data at $T=$const lie on a curve which intercepts the $H=0$ axis at $\chi_{\rm eq}$ [see Eq. (1)]. The initial slope of the curve equals A_3. At decreasing T, A_3 decreases rapidly and, for a given H/T range, strong deviations from the initial slope appear due to the rapid increase of the $H^4, H^6, \ldots$, terms of M/H. At low T, A_3 must be deduced from low-field data (i.e., where M is small): below 100 Oe at 6 K. This is all the more

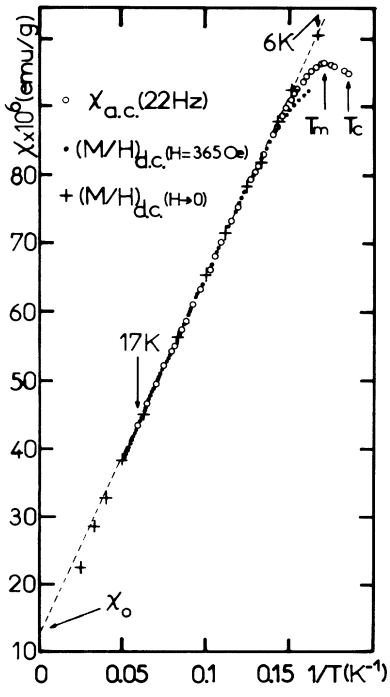

FIG. 1. Susceptibility data vs $1/T$.

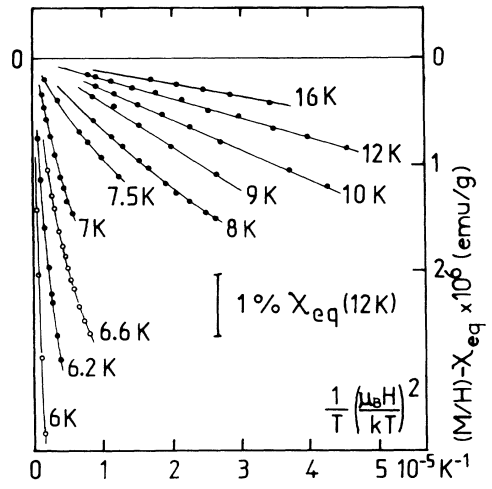

FIG. 2. M/H vs H^2/T^3. We subtract $\chi_{eq}(T)$ to M/H to show all the data in the same figure. $\chi_{eq}(T)$ corresponds to the crosses in Fig. 1.

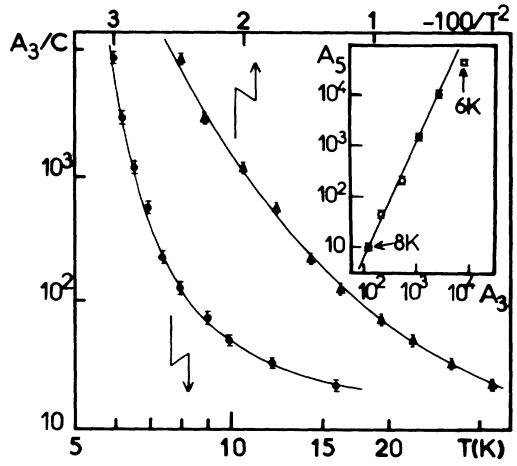

FIG. 3. $\log(A_3/C)$ vs $\log(T)$ and vs $1/T^2$. A_5 is shown to be a power of A_3 in the log-log inset.

difficult since A_3 has to be obtained from the first 1% deviations of M to $\chi_{eq}H$ [see the segment representing 1% χ_{eq}(12 K) in Fig. 2]. It requires a relative accuracy better than 1 part in 10^3 for H, M, and T. To obtain accurate values of χ_{eq}, A_3, and A_5 in the $H=0$ limit at low T, we use a least-squares polynomial fit of M/H vs H^2 up to moderate fields (<500 Oe) where our accuracy is much better. $A_3(T)/C$ is plotted versus T in Fig. 3. The vertical bars indicate the relative error ($<10\%$) on A_3.

The existence of a phase transition is suggested by the drastic variation of $A_3(T)$ and $A_5(T)$. First, to check that A_3 and A_5 are powers of the same quantity $\xi(T)$, we plot A_5 vs A_3 in the log-log plot inset of Fig. 3. Except for the $T=6$-K data, less accurate because they were obtained at very low fields, the points lie on a straight line of slope $S=2.3$ over several decades of A_3 and A_5. When we identify S with $2+\gamma/\beta$ [see Eq. (2)] we obtain $\beta=0.3\gamma$. The next step is to deduce T_c. First, no laws proposed for $d \leq d_c$ fit the data. In Fig. 3 the data do not lie on a straight line over any range of temperature in the plots: $\log(A_3)$ vs $\log(T)$ and $\log(A_3)$ vs $1/T^2$ which correspond, respectively, to the $d<d_c$ and $d=d_c$ predictions. Equation (2) applies for $d>d_c$. At given T_c, the least-squared linear fit of $Y=\log(A_3/C)$ vs $\log(t)$ provides γ, B, and the error E^2 [$=\langle(Y_i - Y_{i\,\mathrm{calc}})^2\rangle$] of the fit. E is reduced significantly by rejecting the data obtained far from T_c, i.e., 12 and 16 K. In the 6–10-K range, E is a minimum for $T_c=5.42$ K (see inset of Fig. 4) leading to $\gamma=3.3$ and $B=3.6$. From $\beta=0.3\gamma$, we find $\beta=1$. In Fig. 4, the data plotted in a $\log(A_3/C)$ and $\log(A_5)$ vs $\log(t)$ diagram for $T_c=5.42$ K lie accurately on straight lines of slope $\gamma=3.3$ and $2\gamma+\beta=7.6$.

We now determine p_{eff}. It equals $(7.4\pm0.4)\mu_B$ given by Eq. (2): $p_{\mathrm{eff}}^2=15$ B, for $An_0=1\pm0.1$. From the Curie constant, we deduce the number $N=4.9\times10^{19}$ moments/g in the sample containing 3.84×10^{21} Mn/g. Thus N equals 1.3% of the Mn concentration, but each moment includes an unknown number of Mn atoms. We now discuss the results.

(i) Many previous fits[9] of χ by a single law $\chi_{eq}=\chi_0+C/(T+\theta)$ over a wide range of T were useful to obtain the order of magnitude of Np_{eff}^2 for studies of the x dependence of χ. They lead to $\theta\neq0$. The refinement

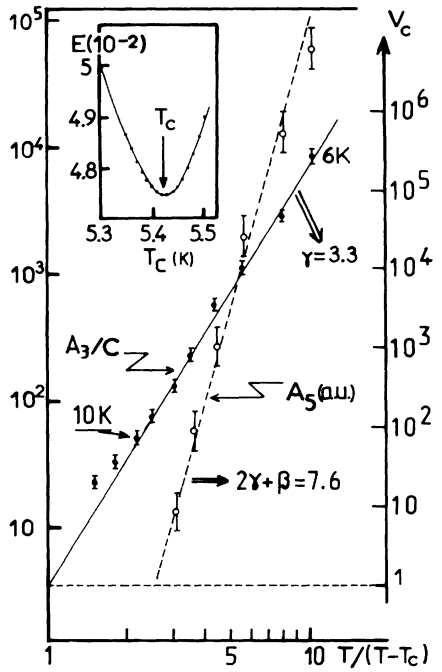

FIG. 4. $\log(A_3/C)$, $\log(A_5/C)$, and $\log(V_c)$ vs $\log[T/(T-5.42\ \mathrm{K})]$. V_c is the correlation volume, to be read using the A_3/C curve. The error E of the fit of $\log(A_3)$ vs $\log(t)$ is shown to be minimum for $T_c=5.42$ K in the inset.

of the analysis allows us to state $\theta=0$ near T_c providing an important result for SG. It means that there are equal weights for the $+J$ and $-J$ interactions. Our argument is all the stronger since we can deduce χ_{eq} down to 6 K, impossible to do with only ac measurements or large dc fields (see above). Deviations from the Curie law are observed above 17 K, in agreement with the general T dependence of θ in interacting paramagnets, already noted[17] in QC. At high T, θ gives the value and the sign of the nearest-neighbor interactions. At decreasing T, θ can change when the spatial range of the interactions increases.

(ii) The correlations can spread over very large distances: the correlation volume $V_c=[(T-T_c)/T]^{-d\nu}$, normalized to 1 for $T=\infty$, can be very large at low T. Since $d\nu=\gamma+2\beta$ we have $V_c=(A_3/B)^{1+2\beta/\gamma}$ and $\nu=1.75$. In Fig. 4, we plot in a vertical scale the values of V_c corresponding to A_3. One notes the huge value of V_c at 6 K: 2.4×10^5 which is, however, much smaller than the typical volume ($\approx 1\ \mu m^3$) of a QC grain. Because of the large value of ν (3 times that of 3D ferromagnets for instance), V_c is large even far from T_c. For example, $V_c=63$ at $T=10\ \mathrm{K}=1.84T_c$.

(iii) $p_{\mathrm{eff}}(7.5\mu_B)$ is larger than in classical SG ($\sim 5\mu_B$ in $CuMn_x$ with $x<1\%$). It can be due to either a cluster of Mn (of course our study cannot give the number of Mn per cluster) or a symmetry-induced moment[18] on Mn in an icosahedral environment resulting in an enhanced density of states at E_F. But the question is are such sites present in the i, decagonal and amorphous phases which exhibit similar magnetic properties? Early studies of diluted alloys[19] interpreted within the clustering assumption show that the Kondo temperature T_K ($T_K>600$ K for a single Mn in Al crystal[19]) is reduced down to zero with increasing number of Kondo impurities per cluster. Since Mn first neighbors are observed[20] in i-$Al_{75}Mn_{21}Si_6$ in contrast with i-$Al_{83}Mn_{17}$, we correlate the increase of the magnetic parameters with the possibility of Mn as nearest neighbors. We reject the hypothesis of moments only due to clusters in QC grain boundaries since the same magnitudes of the parameters are observed in amorphous phases. Finally, the substitution of Mn by Fe, for instance,[21] to deduce p_{eff} may affect the moment of remaining Mn: What then is the moment of a MnFe cluster?

We have shown that the QC $Al_{73}Mn_{21}Si_6$ is a true three-dimensional spin glass with a very small fraction (1.3% of the nominal Mn concentration) of magnetic moments. Indeed, T_c is finite and the values of γ, β, and ν are similar to those found in other $d=3$ SG. We note that T_m(22 Hz) is close to but larger than T_c as in other SG, due to critical dynamics effects (see Fig. 1). In addition, we suggest that the QC is a RKKY spin glass: It exhibits a similar phase transition and $T_m(\omega\approx 100\ \mathrm{Hz})\approx T_c\sim\langle J\rangle$ follows a variation with Np_{eff}^2 (given, for instance, by the specific heat[8] $T_m\sim C_H^{0.8}$) similar to that found in $CuMn_x$ and $AuFe_x$ ($T_m\sim x^{0.7}$). Indeed, in the case of $1/R^3$ magnetic interactions: $\langle J\rangle\sim p_{\mathrm{eff}}^2\langle 1/R^3\rangle$ and $\langle 1/R^2\rangle\sim N$. But in contrast with canonical low-concentrated SG, the value of p_{eff} is larger than that expected for a single magnetic Mn in metals.

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[1]J. J. Hauser, H. S. Chen, and J. V. Waszczak, Phys. Rev. B **33**, 3577 (1986).

[2]C. Berger, J. C. Lasjaunias, J. L. Tholence, D. Pavuna, and P. Germi, Phys. Rev. B **37**, 6525 (1988).

[3]K. Fukamichi, T. Goto, T. Masumoto, T. Sakakibara, M. Oguchi, and S. Todo, J. Phys. F **17**, 743 (1987).

[4]J. J. Hauser, H. S. Chen, G. P. Espinosa, and J. V. Waszczak, Phys. Rev. B **34**, 4674 (1986).

[5]W. W. Warren, H. S. Chen, and G. P. Espinosa, Phys. Rev. B **34**, 4902 (1986).

[6]R. Bellissent, F. Hippert, P. Monod, and F. Vigneron, Phys. Rev. B **36**, 5540 (1987).

[7]D. Fiorani, J. L. Tholence, and J. L. Dormann, J. Phys. C **19**, 5495 (1986).

[8]C. Berger, K. Hasselbach, J. C. Lasjaunias, C. Paulsen, and P. Germi, J. Less Common Metals **145**, 565 (1988).

[9]See references in Z. M. Stadnik, G. Stroink, H. Ma, and G. Williams, Phys. Rev. B **39**, 9797 (1989).

[10]K. Wang, P. Garoche, and Y. Calvayrac, J. Phys. C **8**, 237 (1988).

[11]R. Omari, J. J. Préjean, and J. Souletie, J. Phys. (Paris) **44**, 1069 (1983).

[12]E. Carré, L. Puech, J. J. Préjean, P. Beauvillian, and J. P. Renard, in *Proceedings of the Heidelberg Colloquium on Glassy Dynamics,* edited by J. L. van Hemmen and I. Morgenstern, Lecture Notes in Physics Vol. 192 (Springer-Verlag, Berlin, 1986), p. 75; E. Carré, thesis, University of Paris, Grenoble, France (unpublished).

[13]A. P. Malozemoff and B. Barbara, J. Appl. Phys. **57**, 3410 (1985).

[14]A. J. Bray, M. A. Moore, and A. P. Young, Phys. Rev. Lett. **56**, 2641 (1986), and references therein.

[15]K. Binder, Z. Phys. B **48**, 319 (1982).

[16]W. L. Mc Millan, J. Phys. C **17**, 3179 (1984).

[17]F. Hippert, P. Monod, R. Bellissent, and F. Vigneron, J. Phys. C **8**, 235 (1988).

[18]M. E. Mc Henry, D. D. Vvedensky, M. E. Eberhart, and R. C. O'Handley, Phys. Rev. B **37**, 10887 (1988).

[19]J. R. Cooper and M. Miljak, J. Phys. F **6**, 2151 (1976).

[20]J. M. Dubois, C. Janot, and M. de Boissieu, in *Proceedings of the ILL Workshop on Quasicrystalline Materials, Grenoble, France,* edited by C. Janot and J. M. Dubois (World Scientific, Singapore, 1988), p. 97; J. M. Dubois and C. Janot, J. Phys. (Paris) **48**, 1981 (1987).

[21]M. Eibschütz, M. E. Lines, H. S. Chen, and J. V. Waszczak, Phys. Rev. Lett. **59**, 2443 (1987).