Nonuniform magnetism and spin-glass properties of an Al-Mn-Si quasicrystal

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Comparison of low-field and high-field (18-T) magnetization of the quasicrystal phase of $Al_{73}Mn_{21}Si_6$ shows that only a fraction (from 12% to 25%) of the Mn atoms have a magnetic moment. Below 5.2 K those moments order into a spin-glass phase which display characteristic irreversible properties which are identical to those of classical metallic spin glasses.

We present a systematic investigation of the magnetic properties of the quasicrystal (QC) and crystalline phases of the alloy $Al_{73}Mn_{21}Si_6$ as a function of the magnetic field up to 18 T and as a function of temperature between room temperature and 1.5 K.

Indeed after the initial discovery[1] of the existence of icosahedral symmetry in this system and related ones, it was soon realized that the Mn atoms had a magnetic character and that the alloys were undergoing a magnetic transition at low temperature, possibly of the spin-glass type.[2] The appearance of a magnetic moment for a Mn atom in the QC phase is very puzzling, since the crystalline ordered phase with the same composition is not magnetic.[2] Our investigation concerns: (i) the initial susceptibility versus temperature, (ii) the saturation magnetization at high field (from this a crude analysis is made, giving the fraction of magnetic Mn atoms and the size of their corresponding moment) and (iii) the magnetization properties below the magnetic transition, which are shown to be identical to those of a classical metallic spin glass.

The two alloys of composition $Al_{73}Mn_{21}Si_6$ were supplied by two independent sources,[3] and for comparison, a crystalline β-phase sample of the same composition was obtained by annealing a piece of one of the QC phase samples for two hours at 700 °C. The main interest in comparing the crystalline β phase with the quasicrystal one is that the former structure does not allow for Mn first neighbors.[4] On the other hand, closer Mn-Mn distances are expected to exist in the QC phase; however, a detailed knowledge of the position of the atoms is still lacking.[5] This difference may be crucial in accounting for the different magnetic character of certain Mn atoms in both phases. A structural study has been made of these samples by neutron diffraction.[6] Using the indexing procedure of Cahn and Gratias,[7] only the QC lines were apparent in the QC phase samples, proving that these materials are single phase in composition. A similar conclusion was reached for the β-phase sample obtained after annealing. The samples were in the form of powder obtained after gently crushing the as-quenched ribbons and sieving through an 80-μm mesh.

The high-field measurements have been performed by an extraction method. Figure 1 represents the static magnetization measurement up to 18 T at 4.2 K of both QC samples, together with the crystalline β-phase sample. The latter displays a linear field dependence, corresponding to a paramagnetic susceptibility of $\chi_\beta = (2.65 \pm 0.1) \times 10^{-6}$ emu/g. This susceptibility is found to be independent of temperature between 4.2 K and room temperature, within the accuracy of our mea-

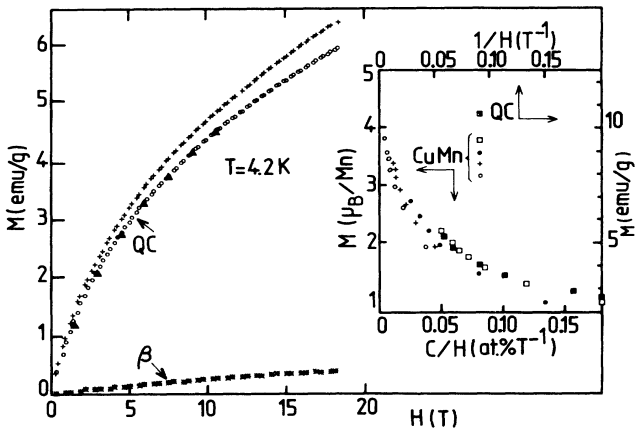

FIG. 1. 4.2-K high-field magnetization of QC and β-crystalline phases of $Al_{73}Mn_{21}Si_6$: (○) Allied Signal Corp. QC sample, (+) Centre de Chimie Métallurgique (CECM) QC sample, (×) β-crystalline phase, obtained after annealing of Allied Signal QC $Al_{73}Mn_{21}Si_6$. At this scale the magnetization curve is reversible. The saturation magnetization (14 emu/g) is determined by scaling with Cu–8 at. % Mn data (closed triangles) from Ref. 11. Inset: Magnetization in μ_B/Mn atom vs, scaled inverse field c/H (at. % T^{-1}) for Cu with 0.2 at. % (□), 0.1 at. % (●), 0.044 at. % (+), and 0.0186 at. % (○) Mn from Ref. 12. The QC phase (■) scales correspond to the right-hand scale (emu/g) and top scale (T^{-1}) of the inset, and have been adjusted to fit on the *Cu*Mn points. From this plot the (extrapolated) value for M_{sat} is 11 emu/g.

surements. This number is one order of magnitude smaller than the reported susceptibility of Ref. 8, and in rough agreement with Ref. 2 for a similar composition. The QC phase samples have a much larger initial susceptibility $\chi_{QC}(4.2\ \text{K})=(1.0\pm0.05)\times10^{-4}$ emu/g, and display a strong curvature towards the field axis. Since our maximum field of 18 T is clearly insufficient to saturate the magnetization, an extrapolation scheme is needed for its evaluation. Assuming[9] a $1/H$ law holds for the high-field magnetization as it approaches saturation, a value of 9.0±0.5 emu/g is obtained for both QC samples. However, since the maximum magnetization we measure is only 6 emu/g, we do not feel safe about this determination, which is certainly an underestimate. Anticipating our comparison with spin-glass magnetic properties, we can make use of the scaling properties of metallic spin glasses, and find the right coordinate changes to map the high-field magnetization curve of Cu-Mn alloys[10] onto our measurements. Such a fit is represented on Fig. 1 with an alloy of Cu–8 at.% Mn (Ref. 11), and the inset of Fig. 1 displays a $1/H$ scaling plot of the magnetization for lower concentration *Cu*Mn alloys.[12] The coincidence of both magnetization curves reflects the fact that the distribution of internal fields is each system is similar. From the known saturation value of the magnetization Cu–8 at.% Mn alloys an estimate of 14±1 emu/g is obtained for M_{sat} for the QC samples. By using the $1/H$ type of fit an (improved) estimate of $M_{sat}=11\pm1$ emu/g is obtained. These two numbers probably bracket the value of the saturation magnetization of our QC samples and will be used in the following analysis.

The initial value of the susceptibility has been measured (in zero external field) by an ac method with a rf field of 1 G at 270 Hz. The results are plotted in Fig. 2. A well-defined cusp is apparent at $T_g=5.2\pm0.1$ K, as already reported in a similar composition QC alloy at 3.5 K.[2] Above this temperature a Curie-Weiss law type of plot $[\chi^{-1}=C^{-1}(T+\Theta)]$ reveal some downward curvature as a function of T, again in accordance with previous analysis of the same kind of data.[2] In the range 5 to 20 K a fit with $p_{eff}=1.25\pm0.1$ μ_B/Mn atom and $\Theta=2.5\pm0.5$ K is possible. If a larger temperature range is retained (30–300 K) a value of $\Theta=15.5\pm1$ K is apparent and a larger value for p_{eff}. However, care should be taken to subtract from the measured χ, a constant, temperature-independent term representing the susceptibility of Al and Si and that of the (unknown) fraction of nonmagnetic Mn. We shall return to this point later.

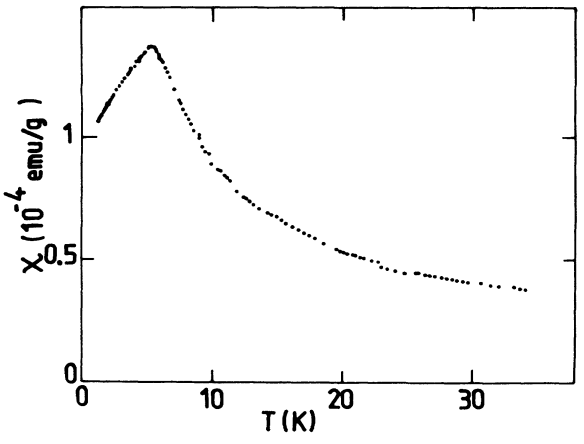

FIG. 2. Zero-field ac (270 Hz) susceptibility of Allied Signal QC phase ($Al_{73}Mn_{21}Si_6$) vs temperature. The susceptibility cusp is at $T_g=5.2\pm0.1$ K. The measurement has been extended up to room temperature in order to determine the Curie constant.

In order to avoid a comparison of the high-field properties to that at low field near T_g where critical spin-glass properties prevail,[13] a measurement of susceptibility (defined by M/H) has been also performed between 5 and 40 K with an extraction method under a 10 kG field. From these results, it is possible to fit a Curie-Weiss law of H/M versus T, yielding p_{eff} (10 kG, 5–40 K)$=1.23\pm0.03$ μ_B/Mn atom and Θ(10 kG, 5–40 K)$=5\pm1$ K. At this point, we note that the calculated value of the saturation magnetization for $p_{eff}=1.23$ μ_B/Mn atom is 23 emu/g. This value corresponds to a spin $S=0.3$ and $g=2.00$ for all Mn atoms in the sample. Thus, although our previous determination of M_{sat} (11 or 14 emu/g) is approximate, we can safely tell that both values are inconsistent with a homogeneous distribution of Mn magnetic moments over all sites.

We now analyze our data by assuming two populations of Mn atoms (magnetic or nonmagnetic) of total number N, in order to get the fraction N^*/N of magnetic Mn atoms and their corresponding spins S^* from the relations: $M_{sat}=N^*g\mu_BS^*$ and $M/H=N^*g^2S^*(S^*+1)\mu_B^2/3k_B(T+\Theta)$. We assume that the g factor$=2.0$, although no spin-resonance signal was visible between 300 and 4.0 K when investigated by ESR at 3.3 kG (9.2 GHz).[14] With $M_{sat}=14$ emu/g we obtain: $N^*/N=0.25\pm0.02$ and $S^*=0.8\pm0.1$. With $M_{sat}=11$ emu/g we obtain: $N^*/N=0.12\pm0.01$ and $S^*=1.3\pm0.1$. We consider that these two sets of values span most probably the situation in our QC compound and show that only a small fraction (12–25%) of Mn sites are magnetic, as already proposed from NMR signal calibrations.[15]

We now turn to the low-temperature magnetic properties of the QC alloys. (Since both sources give the same results, only those from the Allied Signal Corp. sample[3] will be displayed.) We have performed the standard tests for spin-glass type of irreversible magnetic properties.[16] Figure 3 represents the magnetization hysteresis curve between ±10 kG at 1.5 K after cooling down in a 10 kG field. The resulting curve appears symmetrical with respect to the field origin and without any discontinuity of the magnetization, closely resembling that of *Au*Fe spin glasses.[16] No measurable remanent magnetization is observed at 4.2 K, whereas at 1.5 K a small remanent moment of 3.6×10^{-2} emu/g is present. We have investigated how this remanent magnetization can be produced, either by field cooling or by cooling in zero-field and applying a field at the lowest temperature. The result appears in Fig. 4, where the upper curve refers to the field-cooled remanent magnetization (TRM, thermoremanent magnetization) and the lower curve is that of the field-induced remanent magnetization (IRM, isothermal remanent magnetization). We observe for all

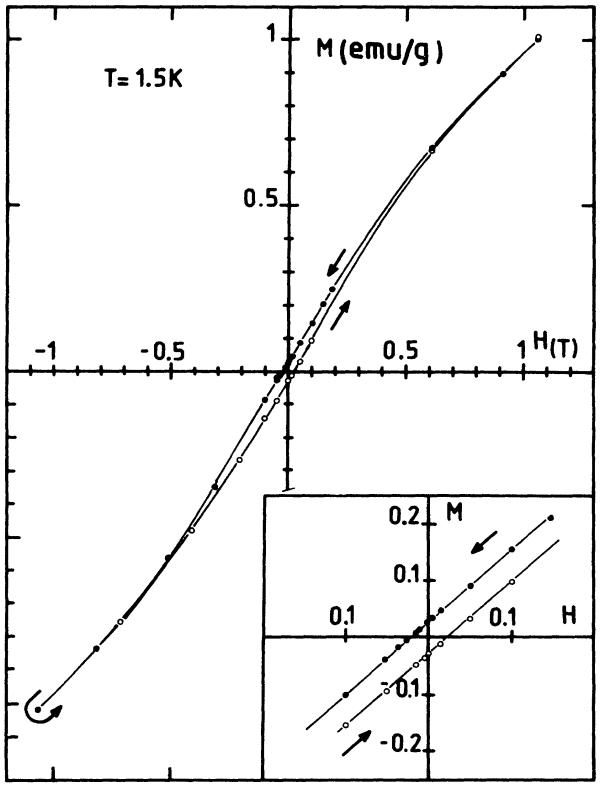

FIG. 3. Magnetic hysteresis of $Al_{23}Mn_{21}Si_6$ QC phase at 1.5 K after cooling in 1 T field. Inset: detail of the remanent magnetization showing symmetry with decreasing or increasing field.

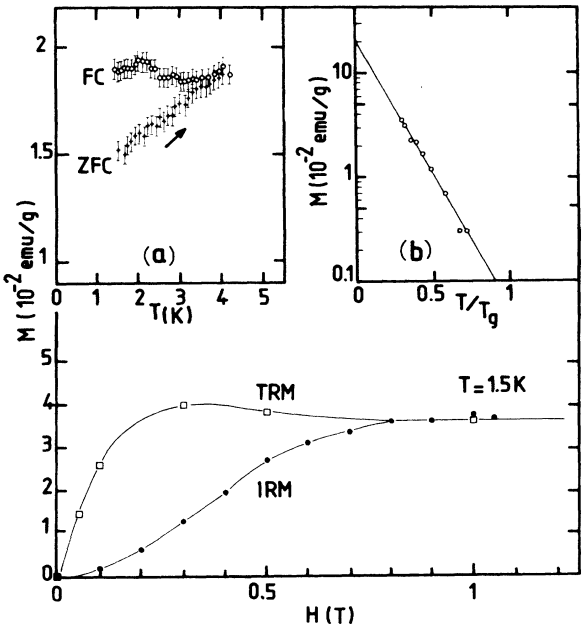

FIG. 4. Remanent magnetization after cooling in zero field and applying a field (IRM) or by cooling in field and removal (TRM) for $Al_{73}Mn_{21}Si_6$ QC phase (Allied Signal) at 1.5 K. Inset: (a) Field-cooled (FC) and zero-field-cooled (ZFC) magnetization for the same alloy for 147 G. (b) Temperature dependence in reduced units of the saturated remanent magnetization.

these magnetization processes a slow decay in time on a logarithmic scale quite typical of classic spin glasses.[11]

The temperature dependence of the saturated remanent magnetization (which corresponds to the plateau above 0.8 T on Fig. 4) is shown in Fig. 4(b) for T between 1.5 and 4.2 K. The solid line is a fit of the form $\exp(-\alpha T/T_g)$ with $\alpha=5.5\pm0.5$. This value is in quantitative agreement with that obtained from other spin glasses.[17] Extrapolating the exponential law to zero temperature yields the maximum value of the saturated remanent magnetization $M_r(0)=0.19$ emu/g. Comparing this value to the saturation value of the magnetization gives for $M_r(0)/M_{sat}$ either 1.7 or 1.4% (respectively, for $M_{sat}=11$ or 14 emu/g), whereas from classical spin glasses the same ratio is always observed to be of the order of 2%.[17] By cooling the QC samples in a field of 147, 500, 1500, 3000, 5000, and 10 000 G, a plateau of magnetization is observed between 4.2 and 1.5 K, thus showing that the magnetization curve (at equilibrium) is temperature independent in this range. A magnetization measurement obtained after zero-field cooling down to 1.5 K and subsequent application of a field of 147 G does not reach the field cooled value of the plateau. We have checked that the difference between the zero-field cooled state and field cooled state is equal to the remanent magnetization after field cooling in 147 G. This property again is found in all classical spin glass systems.[16] Upon warming to 4.2 K, the zero-field cooled state merges with the field cooled one, as it should [see Fig. 4(a)]. Lastly, by taking the fraction N^*/N of magnetic Mn atoms equal to 0.25 or 0.12, the effective magnetic concentration of Mn becomes 5.3 or 2.5%. This yields, respectively, 1 and 2.1 K at. % for the increment of the spin-glass temperature per at. % Mn. This value is observed to be somewhat less than for the corresponding Mn spin glasses in the same concentration range (12 K/at. % for *Cu*Mn; 6 K/at. % for *Ag*Mn). Although any of these tests taken separately is not unequivocal in general, the quantitative overall agreement with the classical spin glasses (*Cu*Mn, *Au*Fe, etc. , . . .) gives support to the presence of a spin-glass state in our quasicrystal phase.

The ensemble of these measurements provides a rather coherent picture of the magnetic properties of $Al_{73}Mn_{21}Si_6$: between room temperature and 5.2 K this system is paramagnetic, characterized by a fraction of Mn sites being magnetic. This fraction is no less than 12 and probably no more than 25%, depending on the determination of the saturated magnetization. The moment attached to this fraction of Mn atoms corresponds, respectively, to 1.6 or 2.6 μ_B/atom, and the Curie-Weiss temperature is 5 K. We can make use of this partition of Mn and assume further that the nonmagnetic Mn atoms in QC phase have the same susceptibility as the nonmagnetic Mn in the crystalline β phase. The knowledge of the fraction N^*/N provides us with a way to analyze (*without new adjustable parameters*) the susceptibility in the higher temperature range (30–300 K). Indeed when correcting for this contribution we find, for $N^*/N=0.25$, $\Theta=4\pm3$ K, and $S=0.7\pm0.1$; and for $N^*/N=0.12$, $\Theta=0\pm3$ K, and $S=2.0\pm0.2$. We consider the agreement between this determination and the

previous values as evidence that the magnetic character of the Mn site is temperature independent in our range of investigation (1.5–300 K). The NMR results of Ref. 15 are more consistent with the determination of the partition of magnetic Mn atoms according to $N^*/N=0.25$, rather than $N^*/N=0.12$. However, care should be taken that the NMR technique only sees the strictly nonmagnetic Mn sites, whereas our measurement determines the magnetic ones. In case of a certain distribution between two possibilities, the NMR determination will always *overestimate* the number of magnetic sites.

Below 5.2 K a spin-glass type of order prevails among the (magnetic) Mn atoms, which display irreversible properties identical to those observed in classical Mn spin glasses. This conclusion implies that the magnetic sites are sufficiently distributed at random to prevent long-range antiferromagnetic or other magnetic order. This model is crude in the sense that it is an extreme picture for the distribution of magnetic character. More work, especially neutron diffraction, is needed to study more precisely the distribution of the magnetic density.

Note added. After this paper was submitted, a paper by F. L. A. Machado *et al.* [Solid State Commun. **61**, 145 (1987)] was published on very similar work. However, their conclusions differ quantitatively from ours in the analysis of the magnetization data (not shown in the above reference). They attribute a "localized magnetic moment of $11\mu_B$ for approximately every 100 Mn atoms" from a fit to a Brillouin function of their data between 15 and 20 K for fields up to 50 kG. Although, qualitatively, they also point out that a large fraction of the Mn atoms are nonmagnetic, the present work offers a more detailed account of the magnetic Mn atoms. A further possible source of our different findings lies in the sample composition, which consists of $Al_{80}Mn_{20}$ in the above reference.

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