Low-temperature magnetism in icosahedral $Al_{70}Mn_9Pd_{21}$

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We report measurements of the specific heat $C_p(T)$, magnetic susceptibility $\chi(T)$, and magnetization $M(H)$ of icosahedral $Al_{70}Mn_9Pd_{21}$ at low temperatures. Below room temperature, the static magnetic susceptibility is well described by a Curie-Weiss-type law above 50 K with a paramagnetic Curie temperature $\Theta = -108$ K, implying fairly strong antiferromagnetic coupling between individual Mn moments. The Curie constant is compatible with a mean effective moment $p_{\text{eff}} = 1.7\ \mu_B$/(Mn atom). The ac susceptibility shows a spin-glass-like maximum at 0.5 K, which, in view of the value of Θ, implies a high degree of frustration. The saturation magnetization and the magnetic specific-heat data below 10 K both indicate a very low concentration of magnetic moments (1.2% of all Mn atoms) as being involved in the spin-glass transition. Comparisons are made with previously reported data for highly frustrated spin glasses.

I. INTRODUCTION

Since the discovery of icosahedral symmetry in rapidly quenched Al-Mn alloys[1] the consequences of quasiperiodicity and possibly related peculiarities of the electronic structure on the physical properties of quasicrystals have been studied intensively. In view of a possible influence of icosahedral symmetry on the local environment of Mn atoms, considerable attention is also paid to the study of magnetic properties of quasicrystals. The metastable quasicrystalline phases Al-Mn and Al-Mn(-Si) show predominantly antiferromagnetic Mn-Mn exchange interactions and possess inhomogeneous magnetic order at low temperatures, typical for canonical spin glasses.[2] Only a small fraction of Mn atoms with a surprisingly low effective magnetic moment appears to be involved in the formation of the spin-glass state, however. Both quantities are considerably enhanced with increasing Mn concentration between 14 and 22 at. %.[3]

Several details of magnetism in quasicrystalline Al-Mn and Al-Mn(-Si) phases are still not clear. The low concentration of magnetic moments exhibiting spin-glass-like behavior at low temperatures indicate a possible magnetic-moment formation on Mn clusters similar to the magnetic behavior of Mn triplets in dilute *Al*Mn alloys,[4] where isolated Mn atoms and Mn pairs are nonmagnetic. Numerous experiments made so far on metastable quasicrystalline phases, which possess a high degree of intrinsic disorder, indicate that their properties, such as the temperature of a spin-glass-like transition, the low-temperature saturation magnetization,[3] nuclear hyperfine specific heat,[5] low-temperature resistivity, and magnetoresistance,[6] are similar to those of corresponding amorphous phases. This implies that the local environment of Mn atoms must be very similar in these materials, and that particular features due to quasiperiodicity cannot be singled out.

New opportunities for experimental studies of the electronic and magnetic properties of quasiperiodic structures are provided with the recent discovery of thermodynamically stable quasicrystals Al-Cu-(Fe,Ru,Os) (Refs. 7–9) and Al-(Mn,Re)-Pd (Refs. 10 and 11) with face-centered icosahedral ordered structure and structural coherence lengths up to 8000 Å (Ref. 12) compatible to those of well ordered crystals. These phases reveal a remarkably low, marginally metallic, electrical conductivity which is fairly well described by calculations considering weak-localization and electron-electron interaction effects.[13–16] The formation of icosahedral phases is usually explained by an analogy to Hume-Rothery-Jones alloys.[17,18] According to this arguing, the icosahedral phase acquires thermodynamic stability, if the Fermi level E_F lies in a pseudogap of the electronic density of states (DOS), which develops when the corresponding Fermi surface reaches the boundary of the zone constructed from the bisecting planes perpendicular to reciprocal quasilattice vectors related to the most intensive x-ray-diffraction peaks.[17] These zones, analogous to the Jones zones in crystals, are nearly spherical in icosahedral quasicrystals due to the high degeneracy of reciprocal quasilattice vectors corresponding to the most intensive x-ray-diffraction peaks. A diplike anomaly in the DOS near E_F was revealed in an icosahedral phase Al-Cu-Fe by photoemission experiments reported in Ref. 19. The low-temperature specific-heat data from Al-Cu-Ru (Ref. 14) and Al-Cu-Fe (Ref. 20) quasicrystals are compatible with distinctly smaller electronic contributions to the specific heat, than the estimated free-electron values, and vary considerably with chemical composition.

Thermodynamically stable Al-Cu-Fe and Al-Mn-Pd phases are the obvious objects for investigating magnetism in quasicrystals. However, the experimental data available so far are controversial and very sensitive to chemical composition and quality of the samples. The low-temperature specific heat and magnetic susceptibility of icosahedral $Al_{65}Cu_{20}Fe_{15}$ both indicate spin-glass-like behavior with a freezing temperature $T_f \approx 1.6$ K.[21] We note that this composition is somewhat different from the most favorable for Al-Cu-Fe quasicrystals. The high-temperature susceptibility of icosahedral $Al_{65}Cu_{20}Fe_{15}$

shows a paramagnetic contribution rising as T^2 up to 800 K.[22] More recently it was reported that annealed icosahedral $Al_{63}Cu_{25}Fe_{12}$ shows a diamagnetic susceptibility varying proportional to $\sqrt{T}$ below 40 K.[13] The large absolute value of the diamagnetic susceptibility, almost twice as high as the value, estimated from contributions of ionic cores, was attributed to a considerable Landau-Peierls diamagnetism caused by a presumably low effective mass. The contribution to the diamagnetic susceptibility varying as $\sqrt{T}$ was ascribed to electron-electron interaction effects. A small paramagnetic contribution observed below 30 K on as-quenched samples was assumed to be due to parasitic phases or structural defects.[13]

The magnetic susceptibility of melt-spun Al-Mn-Pd with Mn concentrations between 7.5 and 10 at. % has been reported by Lanco *et al.*[15] At high temperatures the phase with 10 at. % Mn shows a Curie-Weiss susceptibility with $\Theta \approx 0.3$ K and $C \approx 0.72 \times 10^{-4}$ emu K/g. The authors interpret their data to imply a low fraction of 0.5% of all Mn sites being magnetic, assuming each magnetic site carrying a moment of $5\mu_B$. Phases with a lower Mn concentration indicate a diamagnetic term to the susceptibility superimposed on a Curie-Weiss contribution. The phase with a Mn concentration of 7.5 at. % shows a diamagnetic term to the susceptibility $\chi_0 = -4.1 \times 10^{-7}$ emu/g, which is also almost twice as large as the expected ionic core contributions. Data of the magnetic susceptibility of melt-spun Al-Mn-Pd quasicrystals with high Mn concentration between 10 and 15 at. % have been reported in Ref. 23. A strong paramagnetic susceptibility was found for $Al_{70}Mn_{15}Pd_{15}$ samples with about 9% of the Mn sites forming a magnetic moment. Moreover, the formation of a giant magnetic moment of $6.3\mu_B$ at each magnetic site was inferred. In the same material, a spin-glass-like maximum of the ac susceptibility was found near 10 K. These data, however, were apparently obtained for samples with metastable phases which, in view of the unfavorable nominal sample composition, is not surprising.[11]

In this paper we describe results of measurements of the specific heat $C_p(T)$, magnetic susceptibility $\chi(T)$, and magnetization $M(H)$ curves on $Al_{70}Mn_9Pd_{21}$. This chemical composition is optimal for the formation of the thermodynamically stable icosahedral phase composition, and the material was synthesized by annealing and subsequent quenching of the ingot.[24]

II. EXPERIMENTAL

The specimen of icosahedral $Al_{70}Mn_9Pd_{21}$ synthesized from 99.997% pure aluminum, 99.9+% pure palladium, and 99.94% pure manganese was arc melted several times to provide homogeneity, annealed for 2 days at 800 °C, and subsequently quenched into water directly from 800 °C. The surface analysis by backscattered electron images confirmed the sample composition and the absence of any inclusions of other phases. Selected area electron-diffraction patterns showed a high degree of order and a low density of phason defects. The high quality of the sample was confirmed by high resistivity values varying from 6700 $\mu\Omega$ cm at 300 K to 7300 $\mu\Omega$ cm at 20 mK, comparable to values reported for stable quasicrystals.[13–15] Details of transport measurements and their results are reported in Ref. 25.

All measurements were done using the same $Al_{70}Mn_9Pd_{21}$ sample. The low-field ac susceptibility was measured by a standard mutual inductance technique in the temperature range between 0.2 and 0.7 K. The amplitude of the primary magnetic field was 0.1 Oe and the measurements were made in the frequency range between 18 and 515 Hz. The in-phase component χ' and the out-of-phase component χ'' were measured simultaneously with a two-phase lock-in amplifier. The impedances of the lock-in amplifier input and the pick-up coil system were matched by means of a low-noise transformer. The static susceptibility between 2 and 300 K was measured by a superconducting quantum interference device magnetometer in an external magnetic field of 2 kOe. With the same equipment, magnetization $M(H)$ curves were measured in the temperature range between 1.9 and 10 K and in magnetic fields up to 50 kOe. The specific heat $C_p(T)$ was measured in the temperature range between 60 mK and 18 K using a relaxation-type method.

III. RESULTS AND ANALYSIS

The complete set of $C_p(T)$ data is shown in Fig. 1 on a double logarithmic plot. The broken line indicates the fit to C_p for $T > 8$ K, assuming that the main contributions are from usual electronic and lattice excitations, i.e.,

$$C_p = \gamma T + \beta T^3 + \delta T^5 , \tag{1}$$

with $\gamma = (9.0 \pm 2.7) \times 10^{-3}$ mJ/g K^2 or (0.41 ± 0.12) mJ/mole K^2, $\beta = (8.8 \pm 0.4) \times 10^{-4}$ mJ/g K^4, which corresponds to a Debye temperature of 362 ± 6 K, and $\delta = (9.2 \pm 1.5) \times 10^{-7}$ mJ/g K^6. Here the uncertainties of the fitted parameters correspond to a relative error of each data point of 1% at the confidence level of 90%. A precise determination of the electronic term meets difficulties, because the excess specific heat, obtained by subtracting electronic and lattice contributions from the C_p data, is relatively large up to 8 K, where the lattice contribution is already much larger than the electronic

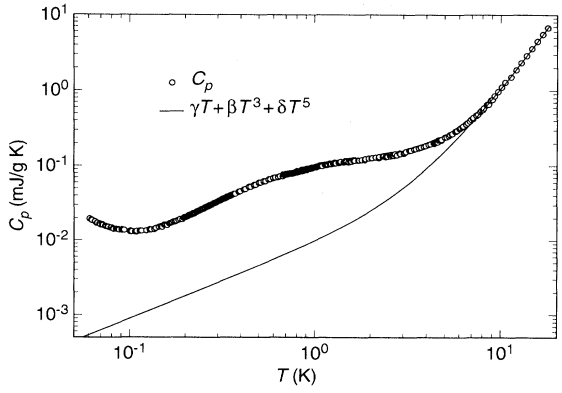

FIG. 1. Specific heat C_p of icosahedral $Al_{70}Mn_9Pd_{21}$ as function of temperature between 0.06 and 18 K.

term. A comparison of the measured value of the electronic specific heat of icosahedral $Al_{70}Mn_9Pd_{21}$ with expectations for a free-electron value is complicated, since the number of electrons, donated by the d-transition element atoms to the conduction band, is not clear. Anyway, we note a very low value of the electronic specific heat which is three times lower than that of aluminum. In the following we analyze the excess specific heat below 8 K.

At the lowest temperatures (below 0.25 K) the excess specific heat, shown on a double logarithmic plot in Fig. 2, was assumed to be the sum of a nuclear hyperfine contribution C_N proportional to T^{-2}, revealing a Schottky anomaly maximum at a temperature considerably below the temperature range of measurements, and a low-temperature spin-glass contribution to the specific heat, which starts off with temperature as T^n, where n is somewhat larger than 1.[26] Hence

$$C_{ex}=aT^{-2}+\alpha T^n \ . \tag{2}$$

A fit between 60 mK and 0.25 K, shown as the solid line in Fig. 2, yields the results $a=(5.8\pm0.05)\times10^{-5}$ mJ K/g or $(2.7\pm0.02)\times10^{-3}$ mJ K/mole, $n=(1.38\pm0.01)$, and $\alpha=(1.64\pm0.03)\times10^{-1}$ mJ/g K$^{2.38}$ or 7.6 ± 0.14 mJ/mole K$^{2.38}$. The broken lines indicate the nuclear hyperfine and spin-glass contributions separately.

A quantitative analysis of the nuclear specific heat C_N is complicated because it may contain contributions due to the hyperfine splitting of the ^{55}Mn, ^{27}Al, and ^{105}Pd nuclear energy levels. Assuming nonetheless that the dominant contribution to the nuclear specific heat C_N is due to an effective magnetic field H_{eff} at the nuclei of magnetic Mn atoms, we may estimate a molar fraction c of all Mn atoms possessing magnetic moments from

$$C_N=cNk_B\frac{I+1}{3I}\left[\frac{\mu_N H_{eff}}{k_B T}\right]^2 , \tag{3}$$

where $I=5/2$ is the nuclear spin of ^{55}Mn. Since the experimental value of H_{eff} for icosahedral $Al_{70}Mn_9Pd_{21}$ is not available, we use the H_{eff} values reported for CuMn, AuMn, and AgMn spin glasses, which lie in the range between 280 and 410 kOe.[27] We estimate $3.1\times10^{-3}<c<7.1\times10^{-3}$. This implies, accounting for the Mn molar fraction of 9 at. %, that between 3.4% and 7.9% of all Mn nuclei experience a sizeable hyperfine field.

The magnetic specific heat C_m obtained by subtracting the nuclear term C_N from the excess specific heat is shown in Fig. 3 as a function of temperature. The magnetic contribution C_m to the specific heat exhibits a broad maximum near 2 K. This temperature is four times higher than the spin-glass freezing temperature $T_f=0.5$ K, determined from the maximum in the $\chi'(T)$ curve shown below (Fig. 6). At the same time, the quantity $C_m/T(=dS_m/dT)$ reaches its maximum very close to the freezing temperature (Fig. 4).

The temperature dependence of the magnetic entropy, obtained from the magnetic contribution C_m to the specific heat as

$$S_m(T)=\int_0^T (C_m/T')dT' \ , \tag{4}$$

reveals that 85% of S_m is developed above the freezing temperature (see Fig. 5). This indicates, that freezing at T_f removes only a small contribution to the magnetic entropy, and implies a considerable short-range order of moments above T_f. This again is a common feature of spin glasses. The magnetic entropy is given by

$$S_m=xN_A k_B \ln(2S_{eff}+1) \ , \tag{5}$$

where x is the molar concentration of magnetic moments involved in forming the spin-glass state and S_{eff} is the effective value of their spin. The magnetic entropy of icosahedral $Al_{70}Mn_9Pd_{21}$ as a function of temperature saturates above 8 K at 12.4 mJ/mole K, thus yielding a value of $x\ln(2S_{eff}+1)=1.5\times10^{-3}$.

The ac susceptibility data are shown in Fig. 6. A relatively broad spin-glass-like maximum in the χ' vs T plot appears at 0.5 K. The variation of the ac susceptibility with external magnetic field (parallel to the excitation field) is also shown in Fig. 6. A 10% reduction of the maximum value of χ' is observed in an external field of 100 Oe. This influence of relatively low external magnetic fields on the ac susceptibility in the temperature range around T_f is typical for spin glasses. We measured χ_{ac} vs temperature curves for several excitation frequencies in the range from 18 to 525 Hz and the χ' vs T curves taken

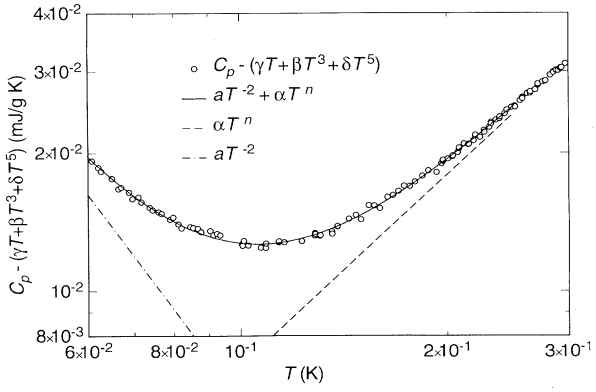

FIG. 2. C_p vs T of icosahedral $Al_{70}Mn_9Pd_{21}$ below 0.3 K.

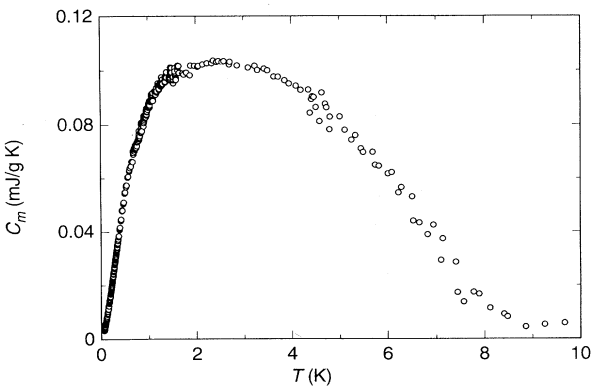

FIG. 3. The magnetic contribution C_m to the total specific heat as function of temperature T.

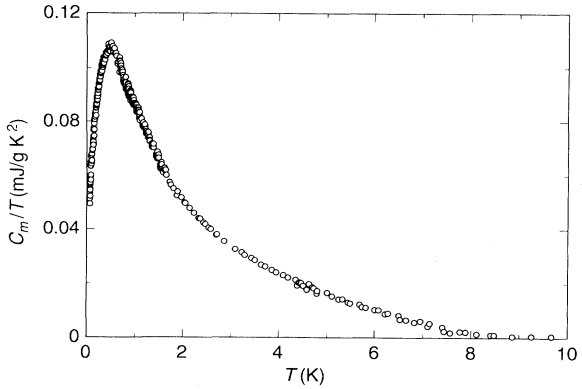

FIG. 4. C_m/T vs T of icosahedral $Al_{70}Mn_9Pd_{21}$.

at 82 and 325 Hz are shown in Fig. 7. With increasing frequency the χ' vs T maxima shift to higher temperatures and broaden, thus again exhibiting typical spin-glass behavior. The variation of the temperature T_f where χ' vs T reaches a maximum by enhancing the excitation frequency f, is plotted in Fig. 8. The T_f vs $1/\ln(f_0/f)$ variation, where $f_0=1\times10^{13}$ s^{-1} was chosen as the characteristic frequency,[28] is, even quantitatively, close to the data reported for a spin glass $Eu_xSr_{1-x}S$ with $x=0.15$.[29] We note a Vogel-Fulcher-type of relaxation behavior

$$f(T_f)=f_0\exp\left[-\frac{E_a}{k_B(T_f-T_0)}\right]. \tag{6}$$

The T_f vs $1/\ln(f_0/f)$ data are reasonably well fitted by a straight line with $T_0=0.07$ K and an activation energy $E_a/k_B=12$ K. The very low value of T_0 as compared to T_f indicates, in fact, that the relaxation behavior is close to an Arrhenius-type. A nearly Arrhenius-type relaxation behavior in spin glasses with short-range interactions has been claimed to indicate a low concentration of magnetic moments.[28] An Arrhenius-type relaxation is also characteristic of metallic spin glasses with a strongly reduced Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[28,29] Magnetic properties of these systems are dominated by short-range interactions.

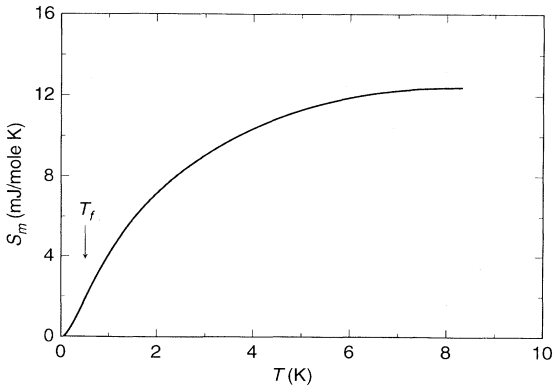

FIG. 5. The magnetic entropy S_m of icosahedral $Al_{70}Mn_9Pd_{21}$ as a function of temperature.

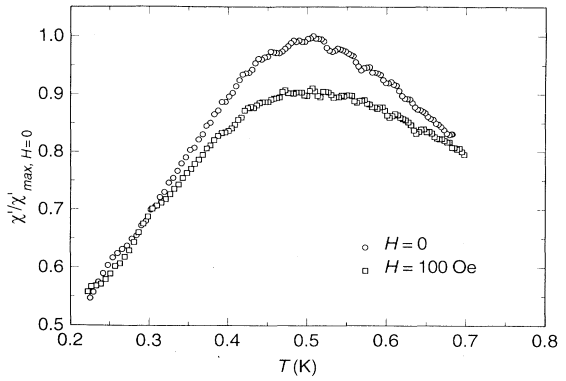

FIG. 6. Low-field ac susceptibility of icosahedral $Al_{70}Mn_9Pd_{21}$ as function of temperature (circles—$H=0$, squares—$H=100$ Oe). The amplitude of the excitation field is 0.1 Oe.

To analyze the static magnetic susceptibility versus temperature we apply a Curie-Weiss law corrected for a temperature-independent susceptibility χ_0 in the form

$$\chi=\chi_0+C/(T-\Theta). \tag{7}$$

A least-squares fit to Eq. (7) in the temperature range between 50 and 150 K yields the values $\chi_0=-2.3\times10^{-5}$ emu/mole for the temperature-independent susceptibility, $C=3.3\times10^{-2}$ emu K/mole for the Curie constant, which is compatible with a mean effective moment $p_{\text{eff}}=1.7\mu_B$/(Mn atom), and $\Theta=-108$ K for the paramagnetic Curie temperature. It is surprising that the value of the mean effective moment mentioned above is so large as compared to the value of magnetic moment per Mn atom that can be inferred from our low-temperature specific-heat and magnetization data (see below). We note that the maximum value of the diamagnetic susceptibility, estimated from contributions of ionic cores is -7.9×10^{-6} emu/mole, i.e., almost three times lower than the fit value of χ_0. The inverse susceptibility,

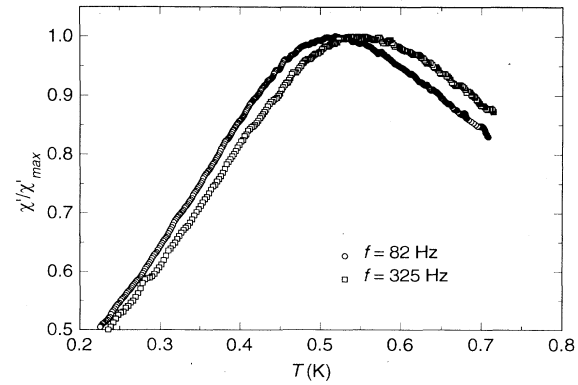

FIG. 7. Low-field ac susceptibility of icosahedral $Al_{70}Mn_9Pd_{21}$ as function of temperature for different frequencies (circles—$f=82$ Hz, squares—$f=325$ Hz). The amplitude of the excitation field is 0.1 Oe.

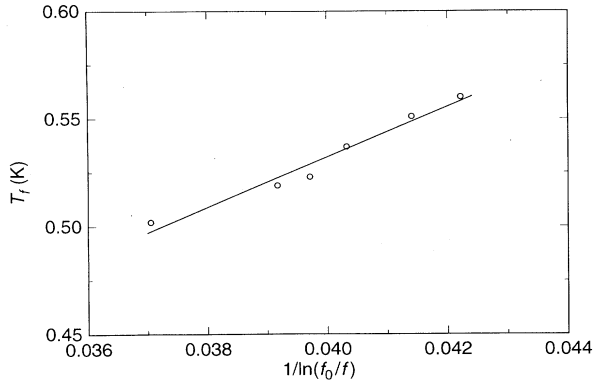

FIG. 8. Frequency dependence of the freezing temperature as deduced from susceptibility maxima.

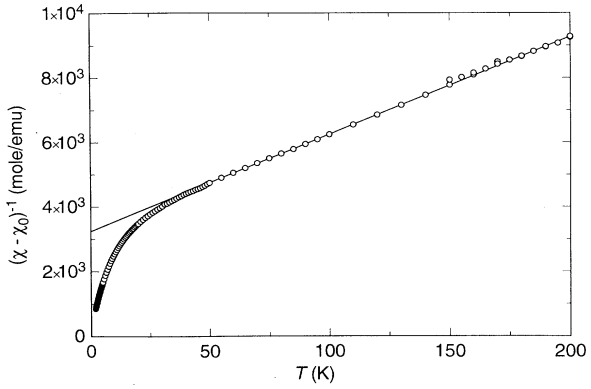

FIG. 9. Inverse magnetic susceptibility χ^{-1} as function of temperature in a field of 2 kOe between 1.9 and 200 K.

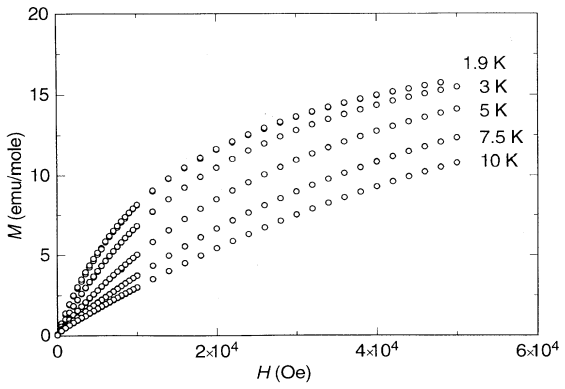

FIG. 10. Magnetization M as a function of field at various temperatures.

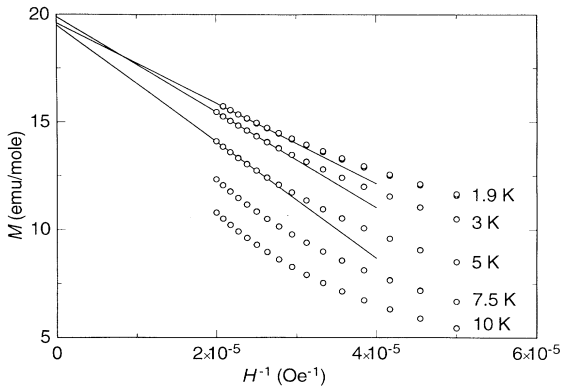

FIG. 11. Magnetization M as a function of inverse field $1/H$.

corrected for the temperature-independent term, $(\chi-\chi_0)^{-1}$ is plotted in Fig. 9 as a function of temperature. Between 10 and 50 K the inverse susceptibility deviates distinctly from the Curie-Weiss behavior, observed as a gradual downturn of the $(\chi-\chi_0)^{-1}$ vs T curve towards the origin. Between 1.9 and 4 K $(\chi-\chi_0)^{-1}$ again approaches a linear variation with temperature and may be fitted by a Curie-Weiss law with parameters that are obviously different from those obtained from the fit above 50 K. In particular the Curie-Weiss temperature is now reduced to $\Theta=-0.54$ K and the mean effective moment to $p_{\text{eff}}=0.47\mu_B/(\text{Mn atom})$.

Magnetization curves M vs H, plotted in Fig. 10, are linear below 2 kOe within the investigated temperature range and clearly show downward curvature at higher magnetic fields. An estimate of the saturation magnetization requires extrapolation to higher magnetic fields, because even at 1.9 K the M vs H plot still exhibits considerable curvature at the maximum available magnetic field of 50 kOe. The saturation magnetization was obtained by plotting M vs $1/H$ (see Fig. 11) and extrapolating the data to infinite field.[30] The zero intercepts of M coincide for the three lowest measuring temperatures 1.9, 3, and 5 K, and we derive for the saturation magnetization $M_s=xN_A\mu_B gS_{\text{eff}}$ a value of 19.7 emu/mole. We consider this value to be quite accurate, since it is only 25% higher than the maximum measured magnetization of 15.7 emu/mole at $T=1.9$ K. From this value of the saturation magnetization, the available magnetic entropy and assuming $g=2$, we derive $S_{\text{eff}}=1.7$ and $x=1.1\times10^{-3}$ [see Eq. (5)].

IV. DISCUSSION

The results presented above imply that icosahedral $Al_{70}Mn_9Pd_{21}$ exhibits the following remarkable thermal and magnetic properties.

The temperature of 2 K, where the magnetic contribution $C_m(T)$ to the specific heat attains a maximum (Fig. 3), is four times higher than the freezing temperature $T_f=0.5$ K. In typical spin glasses C_m is reported to reach a maximum at temperatures only 20–30 % above T_f.[31] However, a few other spin glasses are known, e.g.,

$Eu_xSr_{1-x}S$ and *Pd*Mn, to exhibit the maximum of C_m at temperatures much higher than "normal."[32-34] As a remarkable feature of the magnetic contribution to the specific heat of icosahedral $Al_{70}Mn_9Pd_{21}$, we note that the temperature derivative of the magnetic entropy dS_m/dT attains its maximum very close to the freezing temperature (Fig. 4). The comparison of $C_m(T)$ and $(dS_m/dT)(T)$ indicates that the freezing of the spins at T_f is associated with a maximum change in the magnetic entropy rather than with a change in magnetic energy.[34] This peculiar behavior of the magnetic specific heat is apparently not typical for spin glasses.[31] However, coincidences of maxima of $(dS_m/dT)(T)$ and $\chi'(T)$ have also been reported for the metallic spin glasses *Pd*Mn (Ref. 34) and *Cu*Mn with 0.083 at. % Mn (Ref. 35). The above-mentioned fact that the freezing of the spins at T_f is associated with a maximum change in magnetic entropy may hint to particular thermodynamics of the spin-glass freezing process in these systems.

The values of the paramagnetic Curie temperature $\Theta=-108$ K and mean effective moment per Mn atom $p_{\text{eff}}=1.7\mu_B$ obtained from a high-temperature fit (above 50 K) to the Curie-Weiss law in the form of Eq. (7) indicate strong antiferromagnetic Mn-Mn interactions. This is consistent with the low value of the saturation magnetization at low temperatures. Below 50 K pronounced deviations in the magnetic susceptibility from a Curie-Weiss law are observed. Notoriously such deviations with decreasing temperature are observed for spin glasses well before a maximum at the freezing temperature T_f is reached and they reflect local magnetic correlations, persisting up to temperatures much higher than T_f. In spin glasses the local magnetic correlations often lead to a second linear region in χ^{-1} vs T plots at lower temperatures, somewhat above T_f, resulting in another Curie-Weiss behavior characterized by different parameters.[36] The differences between the values of p_{eff} and Θ obtained from either high- or low-temperature fits are usually much smaller than what we obtained for icosahedral $Al_{70}Mn_9Pd_{21}$. A considerable reduction of the mean effective magnetic moment from $1.7\mu_B$ at high temperatures to $0.47\mu_B$ at low temperatures may be attributed to the formation of nearly compensated antiferromagnetic clusters.[37] The large nuclear specific heat C_N compatible with a concentration c of Mn atoms possessing magnetic moments, which is at least 3 times higher than the concentration of magnetic moments x involved in the formation of the spin-glass state, is an additional experimental indication suggesting antiferromagnetic cluster formation in icosahedral $Al_{70}Mn_9Pd_{21}$.

Similar χ^{-1} vs T behavior as reported above for icosahedral $Al_{70}Mn_9Pd_{21}$, i.e., the existence of a second temperature range, where a reasonably good fit to a Curie-Weiss law can be obtained, and where the respective values of p_{eff} and Θ are considerably lower in the low-temperature limit, is particularly pronounced in spin-glass systems with strong antiferromagnetic interactions, where frustration plays an important role. Examples are Mn- and Co-aluminosilicate glasses $MnO\cdot Al_2O_3\cdot SiO_2$ and $CoO\cdot Al_2O_3\cdot SiO_2$,[36] modified pyrochlore with fcc structure $CsNiFeF_6$,[37] and the layered compound $SrCr_{8-x}Ga_{4+x}O_{19}$.[38] The high degree of frustration in these systems leads to a strong suppression of the freezing temperature as compared to $|\Theta|$, obtained in the high-temperature fit. Icosahedral $Al_{70}Mn_9Pd_{21}$ with $\Theta=-108$ K and $T_f=0.5$ K yields $|\Theta|/T_f=208$, which is higher than the value of $|\Theta|/T_f=150$ reported for $SrCr_8Ga_4O_{19}$,[38] the system possessing, to our knowledge, the highest degree of frustration so far. The very high value of Θ/T_f in $SrCr_8Ga_4O_{19}$ was attributed to the two-dimensional character of the crystal structure, containing planes of Cr^{3+} ions ($S=3/2$) arranged on a Kagomé lattice. For comparison, the most frustrated three-dimensional system $CsNiFeF_6$ reported until now, where magnetic ions occupy positions which form an infinite network of corner-sharing tetrahedrons, is characterized by a value of $|\Theta|/T_f=48$.[37] It is surprising that the ratio $|\Theta|/T_f$ observed for icosahedral $Al_{70}Mn_9Pd_{21}$ is so much higher than for the amorphous system $MnO\cdot Al_2O_3\cdot SiO_2$ ($|\Theta|/T_f=25$) (Ref. 36) with a similar value of the Curie-Weiss temperature $\Theta=-117$ K and, thus, similar strength of antiferromagnetic exchange interactions. This may indicate that the frustration of magnetic moments plays a very important role in forming a spin-glass state in icosahedral $Al_{70}Mn_9Pd_{21}$.

It is difficult to make definitive conclusions concerning magnetic interactions in icosahedral $Al_{70}Mn_9Pd_{21}$. As in canonical spin glasses, the local magnetic moments in icosahedral $Al_{70}Mn_9Pd_{21}$ are coupled through the indirect RKKY exchange interaction. The RKKY interaction in icosahedral $Al_{70}Mn_9Pd_{21}$ is expected to be modified by a random-phase shift in the oscillations, associated with the scattering of electrons.[39] This effect is not important for canonical spin glasses in which the mean free path l is of the order of $c^{-2/3}r_0$,[40] where c is the molar concentration of magnetic moments, and r_0 is a typical separation between them. Since in canonical spin glasses $c\ll 1$ and, therefore, $l\gg r_0$, the RKKY interaction remains unchanged for the physically important distances comparable to r_0. In weakly disordered metals, $l\gg k_F^{-1}$, and in case of low concentrations of magnetic moments with $r_0\gg l$, the typical strength of the RKKY interaction falls as a power law of the spin-separation distance as in pure metals and is mean-free-path independent.[41] The interaction strength in weakly disordered metals, however, is expected to be mean-free-path dependent in the intermediate regime $r_0\sim l$.[42] We note that these results for weakly disordered metals may have to be modified if applied to icosahedral $Al_{70}Mn_9Pd_{21}$, because the condition for weak disorder $l\gg k_F^{-1}$ is not satisfied. Indeed, we can estimate k_Fl from $k_Fl=3mD/\hbar$ where D is the electron diffusion constant. The latter can be derived from the conductivity equation $\sigma(0)=e^2N(E_F)D$. Our conductivity data of icosahedral $Al_{70}Mn_9Pd_{21}$ and the density of states $N(E_F)$ obtained from our specific-heat measurements yield $k_Fl\sim 0.2$. Damping of RKKY interaction may also be caused by spin-orbit-interaction effects.[42] The root-mean-square interaction is expected to be suppressed due to spin-flip scattering on a scale of the

spin-orbit diffusion length $L_{so}=\sqrt{3D\tau_{so}}$. The spin-orbit scattering time $\tau_{so}\sim 1.3\times 10^{-13}$ s determined from the transport measurements[25] performed on the same sample is compatible with $L_{so}\sim 17$ Å. The concentration of magnetic moments involved in the spin-glass transition ~ 0.11 at. % yields $r_0\sim 24$ Å. Therefore, in icosahedral $Al_{70}Mn_9Pd_{21}$ $L_{so}\sim r_0$ and the typical strength of the RKKY interaction may thus be modified by the spin-orbit scattering.

Concerning the atomic structure of icosahedral Al-Mn-Pd, so far only a crude model has been derived from neutron and x-ray-diffraction data obtained on a single quasicrystal.[43] This model is a first approximation which corresponds to a minimum "hard core" common to all other possible structure models. Within the framework of this model a three-dimensional structure of icosahedral Al-Mn-Pd can be described by a quasiperiodic arrangement of icosahedral structure units[44] with additional "adhesive" atoms between them. External shells of these icosahedral structure units are similar to those of the Mackay icosahedron. The Mackay icosahedron or fractions of it are also present in the metastable Al-Mn(-Si) quasicrystal as suggested by the structure models of Duneau and Oguey[45] and Janot *et al.*[46] The structure model of icosahedral Al-Mn-Pd implies the presence of two icosahedral structure units with different chemical decorations, which is consistent with the observed face-centered icosahedral superstructure. The large icosahedron of the icosahedral structure unit is decorated by Mn with a small fraction of either Pd or Al. In turn, the icosidodecahedron is decorated by either Al or simultaneously Al and Pd. For comparison, the large icosahedron of the Mackay icosahedron is decorated by Mn only and the icosidodecahedron is decorated exclusively by Al. Although the structure model of icosahedral Al-Mn-Pd proposed in Ref. 43 gives a reasonable atomic decoration of the quasilattice, the actual positions of the Mn atoms are not known in detail. However, an icosahedral quasilattice containing magnetic moments very likely allows for a high degree of frustration, since magnetic moments may become frustrated due to an icosahedral symmetry of the structure units and because equivalent sites in icosahedral structure units are not equivalent in the quasilattice.

As we mentioned above, the low concentration of magnetic moments in metastable Al-Mn(-Si) quasicrystals as compared to the molar fraction of Mn was attributed to magnetic-moment formation on Mn clusters. An alternative description of icosahedral $Al_{70}Mn_9Pd_{21}$ as a system with a high Kondo temperature for single Mn atoms and successively decreasing Kondo temperatures for Mn atoms having one or more Mn nearest neighbors (Kondo glass[47]) seems to be irrelevant. The very small linear term to the specific heat at $T\gg T_f$ derived from our specific-heat data (Fig. 1) rules out any sizeable contribution due to Kondo effect. Also, it is very unlikely that 9 at. % of Mn in icosahedral $Al_{70}Mn_9Pd_{21}$ can be compensated by interaction with conduction electrons, especially taking into account the low density of states at the Fermi level E_F indicated by the small electronic contribution to the specific heat.

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