Mn magnetism in icosahedral quasicrystalline $Al_{72.4}Pd_{20.5}Mn_{7.1}$

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The unusual magnetism of manganese atoms in an icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ single-grain quasicrystal was studied by ^{27}Al nuclear magnetic resonance (NMR), magnetic susceptibility, and electrical resistivity measurements. Between room temperature and 50 K both the ^{27}Al NMR linewidth and the frequency shift exhibit a Curie-Weiss-type, $1/(T-\theta)$ temperature dependence. At lower temperatures a significant narrowing of the linewidth, concomitant with a reduction of the frequency shift is observed. These features can be explained by a gradual reduction of the local exchange magnetic field at the position of the ^{27}Al nuclei that is transferred from the manganese *d* moments via the conduction electrons. Two possible origins of this phenomenon are discussed: (i) the Kondo-like screening of manganese moments by the conduction electrons and (ii) the ''resistivity''-damping of the RKKY interaction due to increasing electron localization at low temperatures.

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I. INTRODUCTION

The interpretation of peculiar magnetic properties of quasicrystalline materials containing *d* transition metal elements, especially Mn atoms, still represents a major controversial issue. Depending on the chemical composition, the structural character, and the concentration of the transition metal element, quasicrystals (QC's) can exhibit diamagnetic,[1,2] paramagnetic,[3] and spin-glass-type[4–6] properties. A particular case is the magnetism of the icosahedral *i*-AlPdMn QC family, where only Mn is expected to carry a localized magnetic moment. It has been shown[5,6] that in structurally perfect *i*-AlPdMn QC's two kinds of Mn sites exist. A large majority of these are nonmagnetic whereas a small fraction (typically about 1%) of the Mn sites carries a large magnetic moment of up to several Bohr magnetons. The appearance of large magnetic moments on only a small fraction of Mn sites, the rest carrying no moment, was theoretically demonstrated to be an intrinsic property of QC structures and their approximants.[7] *Ab initio* calculations for AlPdMn periodic approximants demonstrated that the appearance of magnetic moments is related to the local atomic coordination around a given Mn site. Large magnetic moments may only form on a small number of Mn sites, which are characterized by a loose coordination of Al atoms and some close Pd neighbors, but no close Mn neighbors. Direct Mn-Pd contacts, which exist in a substantial number only on a few Mn sites, lead to a locally enhanced Mn-*d*−Pd-*d* hybridization and repulsion between the nearly full Pd-*d* band and the half-filled Mn-*d* band, thus promoting moment formation. Recently it was claimed,[8] however, that an effective Mn-Mn interaction mediated by the conduction electrons plays a major role in the formation of the Mn moments. It was also suggested[6] that the lack of magnetic moments on most of the Mn sites does not originate from a Kondo-type screening of moments by conduction electrons because of the low density of electronic states at the Fermi energy.

The magnetic properties of *i*-AlPdMn QC's vary strongly with the Mn concentration. For $Al_{68.7}Pd_{21.7}Mn_{9.6}$ (Ref. 6) the magnetic interactions between the Mn moments result in a spin glass ordering below $T_g = 1.1$ K. An only insignificantly smaller Mn concentration results in a considerable reduction of the spin glass transition temperature T_g to 0.5 K for $Al_{70}Pd_{21}Mn_9$ (Ref. 5). For *i*-AlPdMn alloys containing less than 8% of Mn, no spin glass transition has been reported as yet. One of the basic problems in the context of magnetism in QC's is to establish the exact nature of coupling between the magnetic moments that determines the macroscopic response with respect to applying external magnetic fields. QC's of the *i*-AlPdMn family exhibit rather low electrical conductivities but it seems reasonable to assume, as a first approximation, that it is the conduction-electron-mediated indirect exchange interaction of the Ruderman-Kittel-Kasuya-Yosida (RKKY)–type, which provides a coupling between localized Mn moments. This assumption encounters two major problems. The first is the lack of translational periodicity of the QC lattices, which leads to the so-called ''disorder''-damping of the RKKY interaction because of random phase shifts in the oscillating conduction-electron spin polarization in the vicinity of magnetic centers,[9–11] thus leading to polarization compensations at individual lattice sites. A consequence of this destructive interference is a

strong reduction of the spatial range of the RKKY interaction. The observation of this RKKY disorder damping was first identified for a polycrystalline AlCuMn alloy by ^{27}Al nuclear magnetic resonance (NMR).[10] It is intriguing that this ternary alloy series also exhibits QC phases in a narrow concentration range. The second problem is caused by the intrinsic criticality of the electron states in QC's, i.e., the nonperiodic lattice does not allow for true Bloch states and the corresponding wave functions exhibit a power-law decay with distance, such that $\psi(r) \propto r^{-\alpha}$. This trend toward localization is likely to cause a substantial reduction of the RKKY interaction as well. Since the enhanced electron localization upon cooling also reduces the conduction electron mean free path, this kind of damping of the RKKY interaction was named the ''mean-free-path''- or ''resistivity''-damping.[9,10]

In this paper we present a study of the magnetic response of an icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ single-grain quasicrystal. The chemical composition implies that this material is situated on the Mn-poor side of the icosahedral AlPdMn phase diagram (the ideal icosahedral composition being $Al_{70}Pd_{22}Mn_8$). The magnetic properties were studied between 3 K and room temperature by recording ^{27}Al NMR line shapes and frequency shifts, as well as by measurements of the magnetic susceptibility and electrical resistivity. At temperatures above 50 K the magnetic properties may fairly well be explained by considering the usual RKKY interaction. Below 50 K, however, some anomalous features have been observed. The transferred hyperfine local magnetic field of the Mn *d* moments monitored at the ^{27}Al sites shows a clear tendency to vanish at low temperatures. Analyzing the data, two possible causes for this effect are considered: (i) a temperature-dependent reduction of the number or the magnitude (or both) of the Mn magnetic moments by some kind of conduction electron screening effect or (ii) a temperature-dependent decrease of the spatial range of the RKKY interaction due to, e.g., an increasing electron localization at low temperatures. The second possibility would result in a reduction of the Mn transferred field at sites in the neighborhood of the magnetic centers even in the case that the number and the magnitude of the Mn moments remain unchanged.

II. EXPERIMENT

All experiments were performed on the same sample with the nominal composition $Al_{72.4}Pd_{20.5}Mn_{7.1}$ (in the following referred to as $AlPdMn_{7.1}$). A large ingot was grown by the Czochralsky technique and was subsequently annealed in vacuum at 800 °C. The monodomain sample was then cut from the ingot and was first used to observe orientation-dependent ^{27}Al NMR spectra in a magnetic field.[12] The same sample has also been used in recent NMR studies of atomic motion[13] and nuclear spin relaxation.[14,15] The room-temperature resistivity of the sample was $\rho = 2040\ \mu\Omega$ cm, of similar value as those reported for other good-quality samples of the *i*-AlPdMn family. The ^{27}Al NMR spectra were obtained by a magnetic-field-sweep technique, the details of which are given in Ref. 12. The irradiation frequency was set to $\nu_0(^{27}\mathrm{Al}) = 26.134$ MHz, corresponding to a center absorption field $B_0 = 2.35$ T. The measurements of the ^{27}Al NMR frequency shift were repeated in a higher field of 6.3 T. Bulk magnetic susceptibility measurements were performed in a Quantum Design superconducting quantum interference device magnetometer equipped with a 5 T magnet.

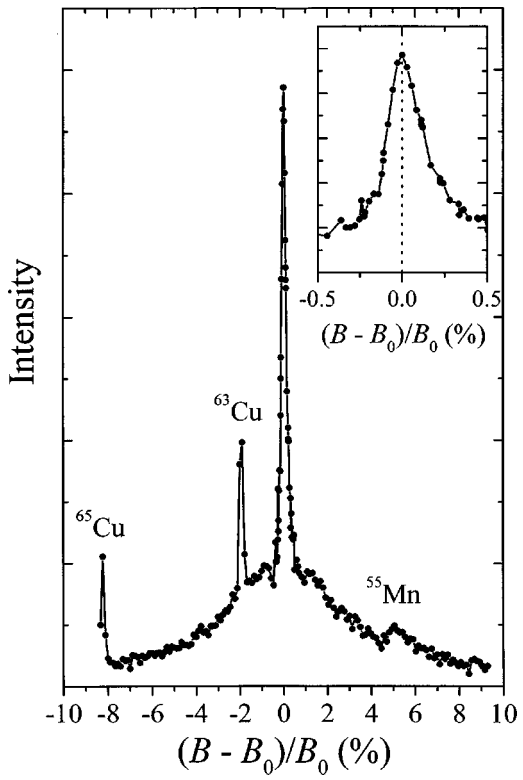

FIG. 1. ^{27}Al field-swept NMR spectrum of a single-grain icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ quasicrystal at room temperature [$\nu_0(^{27}\mathrm{Al}) = 26.134$ MHz, $B_0 = 2.35$ T, fivefold axis oriented perpendicular to B_0]. The inset shows the central line on an expanded scale. The ^{63}Cu and ^{65}Cu lines originate from the copper wire of the probehead coil.

III. RESULTS

A. ^{27}Al NMR spectrum and the frequency shift

The room temperature ^{27}Al NMR spectrum of our $AlPdMn_{7.1}$ sample is displayed in Fig. 1 for the orientation where the fivefold axis is oriented perpendicular to the magnetic field. The spectrum exhibits a typical powderlike structure of a spin $I = \frac{5}{2}$ nucleus with a substantial inhomogeneous broadening, extending in total over about 4700 G. The broad ''background'' signal represents first-order quadrupole-perturbed satellite transitions ($\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$ and $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$),[12,16] whereas the narrow, high-intensity central line represents the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition that is quadrupole-perturbed in second order only. Three additional resonances are superimposed on the ^{27}Al spectrum. The ^{55}Mn line, which is observed at its Zeeman frequency, reveals that nonmagnetic Mn sites must exist in this sample. The resonances of the magnetic Mn atoms are so strongly paramagnetically shifted that they are not observed. The other two additional resonances are the ^{63}Cu and ^{65}Cu lines that originate from the copper wire of

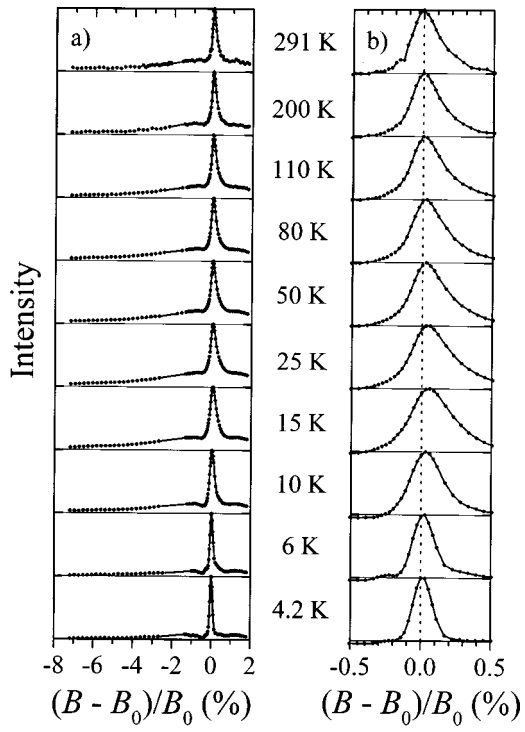

FIG. 2. (a) Temperature dependence of the ^{27}Al field-swept NMR spectra of $Al_{72.4}Pd_{20.5}Mn_{7.1}$. The spectra are scaled to the same height on the vertical axis and the ^{63}Cu line at $(B-B_0)/B_0 \approx -2\%$ was cut out. (b) Temperature dependence of the central line on an expanded scale.

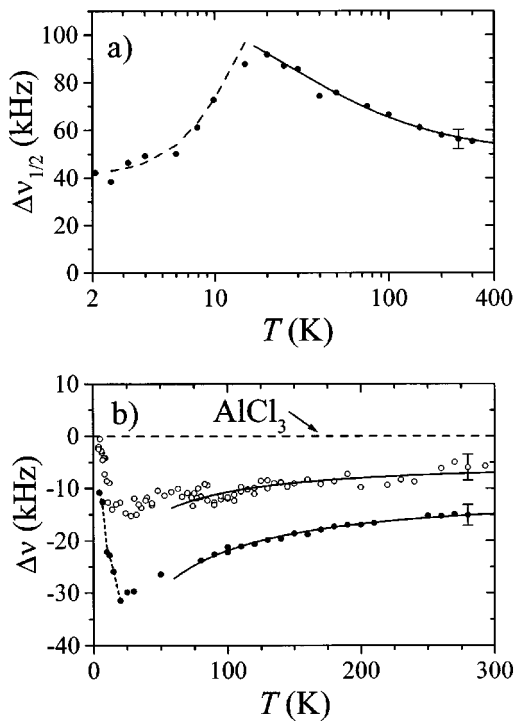

FIG. 3. (a) Temperature dependence of the FWHM $\Delta\nu_{1/2}$ of the ^{27}Al central line shown in Fig. 2(a) and (b) the frequency shift $\Delta\nu$ of the central line measured in two fields: 2.35 T (solid circles) and 6.3 T (open circles). Solid lines are Curie-Weiss fits of the data for temperatures above 50 K discussed in the text, whereas the dashed line is a guide for the eye.

the probehead coil. Although the ^{27}Al spectrum is obtained from measurements using a monodomain $AlPdMn_{7.1}$ sample, it exhibits only a slight orientation dependence and its shape is not much different from the $I=\frac{5}{2}$ spectrum of a crystalline powder.[12] Since the powder spectrum extends in total over the frequency interval of $4\nu_Q$, where $\nu_Q=3e^2qQ/20h$ is the quadrupole coupling constant, the spectrum of Fig. 1 yields $\nu_Q \approx 1.31$ MHz or 1190 G in magnetic-field units. As may be seen in the inset of Fig. 1, the ^{27}Al central line is asymmetric.

A selection of ^{27}Al NMR spectra, measured as a function of temperature in the interval between 300 and 3 K is displayed in Fig. 2(a). The amplitudes have been scaled to the same value on the vertical axis. In order to emphasize the unusual behavior of the central line, the central line signals were extracted from the total spectra [Fig. 2(b)] by fitting the satellite intensity with a Gaussian and subtracting it from the measured spectra. From room temperature to 20 K the central line broadens continuously with decreasing temperature, whereas below 20 K an unexpected and substantial narrowing is observed. The full width at half maximum (FWHM) $\Delta\nu_{1/2}$ of the central line, as a function of temperature, is shown in Fig. 3(a). Upon cooling from 300 to 20 K, $\Delta\nu_{1/2}$ increases proportionally to $1/T$. Just below 20 K, $\Delta\nu_{1/2}(T)$ passes through a maximum, followed by a rapid decrease upon further cooling down to 3 K. The total line narrowing is quite remarkable. The width changes from 95 kHz at 19 K to 40 kHz at 3 K, i.e., by a factor of 2.4. Apart from some intensity variations, to be discussed below, no substantial changes were observed in the satellite part of the spectrum.

A similar unusual behavior is encountered in the temperature dependence of the frequency shift $\Delta\nu=\nu-\nu_L$ of the ^{27}Al central line position, where ν_L denotes the ^{27}Al resonance frequency in an aqueous solution of $AlCl_3$. The ^{27}Al shift in $AlPdMn_{7.1}$ is found to be small and negative, exhibiting an unusual temperature dependence as shown in Fig. 3(b). At room temperature the shift $\Delta\nu/\nu_L$ measured in a field of 2.35 T amounts to -5.7×10^{-4}. Upon cooling $|\Delta\nu/\nu_L|$ follows a $1/T$ dependence down to 20 K where it reaches its largest negative value -1.1×10^{-3}. Below 20 K the absolute value of the shift starts to decrease in very much the same manner as the linewidth. The total reduction of the shift from 20 to 4 K is by a factor of 1.9. The measurement of the shift was repeated in a three-times higher field of 6.3 T and the absolute value of the shift was found to be reduced to one third of its low-field value.

The measured ^{27}Al spectra, shown in rescaled form in Fig. 2(a) indicate that the narrowing of the central line below 20 K is accompanied by a growth of its height, so that its integrated intensity (the area under the curve) remains constant with temperature. Since the spectra are displayed in the form of constant-height plots, it appears as if the satellite intensity would decrease with decreasing temperature. Here it is important to consider the possible trivial explanation of the unusual narrowing phenomenon in terms of the ''all-or-nothing'' intensity wipe out, where the frequency shifts of

the strongly perturbed ^{27}Al nuclei could be so large that their contribution to the signal falls outside of the observable frequency window. In case of temperature-dependent shifts, as they are in our case, a continuous loss of the spectral intensity upon cooling would be observed below a temperature where the frequency shifts become larger than the frequency observation window of the NMR line-shape experiment. The residual intensity at the lowest temperature would then originate from the unperturbed nuclei only, thus producing a narrow line with a smaller average shift, but with strongly reduced intensity. In our case this scenario can be ruled out by a simple argument. The frequency observation window of our line-shape experiment extends over 5.2 MHz (or 4700 G, see Fig. 1), whereas the ^{27}Al central line starts to narrow below 20 K where it reaches its largest width $\Delta\nu_{1/2}=95$ kHz. This $\Delta\nu_{1/2}$ value amounts to a tiny fraction of 1.8% of the observation window only, so that the frequency shifts are definitely small in comparison with the window size. This argument confirms that the unusual temperature dependence of the ^{27}Al spectra in Fig. 2 cannot be accounted for by the trivial explanation of the ''all-or-nothing'' intensity wipe out. Instead, the reductions of both the linewidth and the frequency shift reflect an unusual magnetism of the $AlPdMn_{7.1}$, to be discussed below after presenting the results on bulk magnetic susceptibility.

B. Magnetic susceptibility

The magnetization and bulk magnetic susceptibility $\chi(T)$ measurements on the $AlPdMn_{7.1}$ sample were performed in the temperature interval from 300 to 2 K in magnetic fields up to 5 T. The results are very similar to previously reported data[1,5,6,17] on *i*-AlPdMn compounds with similar compositions. The M/H ratio contains both a diamagnetic and a paramagnetic contribution, which, in the high-temperature regime, can be described by

$$\chi=\chi_d+\frac{C}{T-\theta}. \tag{1}$$

The M/H data, measured in a field of 2000 G where M varies linearly with H, were analyzed with Eq. (1). The fit to the data points at temperatures $T>50$ K yielded a diamagnetic susceptibility $\chi_d=-1.38\times10^{-5}$ emu/mole of sample, $C=3.2\times10^{-2}$ emu K/mole of Mn and $\theta=-26$ K. The negative Curie-Weiss temperature θ suggests a predominantly antiferromagnetic-type coupling between the Mn d electron moments. The paramagnetic susceptibility $\chi-\chi_d$ is displayed in Fig. 4 for temperatures between 2 and 120 K, where it may be seen to follow a Curie-Weiss-type law at temperatures above 50 K. Below this temperature we note a continuously increasing deviation from the high-temperature behavior. The significance of this feature is discussed in Sec. IV.

Earlier specific-heat and magnetic susceptibility measurements on different *i*-AlPdMn samples[5,6] have established quite generally that within this family of QC's, only a fraction of about 1% of the Mn atoms carries a magnetic moment. This conclusion is also valid for our $AlPdMn_{7.1}$

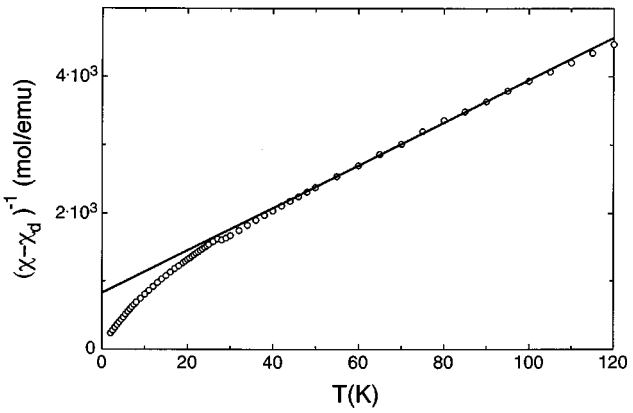

FIG. 4. Temperature dependence of the paramagnetic susceptibility $\chi-\chi_d$ of the $Al_{72.4}Pd_{20.5}Mn_{7.1}$ in a field $H=2000$ G. The solid line is a Curie-Weiss $C/(T-\theta)$ fit with $\theta=-26$ K.

sample, as it follows from the analysis of the Curie-Weiss constant C that yields an experimental value of the mean effective moment $p_{\rm eff}^{(\rm exp)}=0.51\mu_B/(\text{Mn atom})$. This low value of $p_{\rm eff}^{(\rm exp)}$ indicates that only a fraction f of all Mn atoms carries localized moments. The mean effective moment per magnetic ion in the regime $k_BT\gg p_{\rm eff}H$ is defined as[18] $p_{\rm eff}=p_{\rm eff}^{(\rm exp)}/\sqrt{f}$, so that the true mean effective moment $p_{\rm eff}$ is larger than the experimentally measured value $p_{\rm eff}^{(\rm exp)}$ by a factor $1/\sqrt{f}$. Unfortunately the actual valence of Mn atoms in the *i*-AlPdMn system is not known, but the $p_{\rm eff}$ values for the three most likely ionic configurations of the Mn ions[19] are all relatively close to $5\mu_B$, i.e., $p_{\rm eff}(Mn^{2+})=5.9\mu_B$, $p_{\rm eff}(Mn^{3+})=5.0\mu_B$ and $p_{\rm eff}(Mn^{4+})=4.0\mu_B$. Assuming that the nonzero Mn moments have an average value of $p_{\rm eff}\approx5\mu_B$, we derive a fraction $f=(p_{\rm eff}^{(\rm exp)}/p_{\rm eff})^2\approx1\%$ of all Mn atoms to carry magnetic moments above 50 K. The high-temperature susceptibility is thus interpreted to indicate that (i) only a small fraction of about 1% of all Mn atoms carries localized magnetic moments, (ii) that these moments have the full magnitude expected for manganese, and (iii) that the number and magnitude of the moments do not change with temperature within the Curie-Weiss regime above 50 K.

IV. DISCUSSION

In order to analyze the origin of the unusual ^{27}Al NMR line narrowing and frequency shift reduction below 20 K in the $AlPdMn_{7.1}$, we now discuss the electric and magnetic interactions of the ^{27}Al nucleus with the surrounding ions and electrons in the QC lattice. The NMR resonance frequency corresponding to the $m\rightarrow m-1$ spin transition of the ith ^{27}Al nucleus ($I=\frac{5}{2}$) can be written as the sum

$$\nu_i(m)-\nu_0=\nu_{{\rm quad},i}^{(1)}(m)+\nu_{{\rm quad},i}^{(2)}(\tfrac{1}{2})+\nu_{{\rm mag},i}+\nu_{{\rm exch},i}, \tag{2}$$

where $\nu_0=\gamma H_0/2\pi$ is the Zeeman frequency and γ is the nuclear gyromagnetic ratio. The term $\nu_{{\rm quad},i}^{(1)}(m)$ is the first-order quadrupole shift that affects any spin transition $m\rightarrow m-1$, except the central ($\frac{1}{2}\rightarrow-\frac{1}{2}$) transition

$$\nu^{(1)}_{\mathrm{quad},i}(m) = -\frac{\nu_{Q,i}}{2}(m-\tfrac{1}{2}) \times (3\cos^2\theta_i - 1 - \eta_i \sin^2\theta_i \cos 2\phi_i). \quad (3)$$

The quadrupole coupling constant $\nu_{Q,i} = 3eq^{(i)}Q/20h$ is given by the largest principal value of the electric field gradient (EFG) tensor at the lattice site i, which can be written as

$$eq^{(i)} = V^{(i)}_{ZZ} = V^{\mathrm{ion}}_{ZZ,i}(1+\gamma^{(i)}_{\infty}) + V^{\mathrm{el}}_{ZZ,i}. \quad (4)$$

The first term on the right-hand side of Eq. (4) originates from the neighboring ionic charges, enhanced by the Sternheimer antishielding factor $\gamma^{(i)}_{\infty}$ due to the ionic electric field polarization of the core electrons. The second term originates from the charges of the conduction electrons. The angles θ_i and ϕ_i in Eq. (3) define the orientation of the EFG tensor principal axis system with respect to the external magnetic field, and η_i is the quadrupole asymmetry parameter. The first-order quadrupole shift is independent of the external magnetic field.

The second-order quadrupolar shift is important only for the central transition, which is not affected by the quadrupolar interaction in first order. It is inversely proportional to the external magnetic field and is written as

$$\nu^{(2)}_{\mathrm{quad},i}(\tfrac{1}{2}) = \frac{\nu^2_{Q,i}}{12\nu_0}\{6\sin^2\theta_i(1-9\cos^2\theta_i) - 4\eta_i\cos 2\phi_i \sin^2\theta_i(9\cos^2\theta_i+1) + \eta_i^2(-\tfrac{16}{3}+8\cos^2\theta_i+6\cos^2 2\phi_i \sin^4\theta_i)\} \quad (5)$$

The term $\nu_{\mathrm{mag},i}$ in Eq. (2) represents the frequency shift due to the magnetic hyperfine coupling between the nuclear spins and the s, p, or d conduction electrons. This shift is the same for all nuclear spin transitions and is linearly proportional to the external field,

$$\nu_{\mathrm{mag},i} = \frac{\gamma}{2\pi}\left[K_i + \frac{K_{Z,i}}{2}(3\cos^2\theta_i - 1 - \varepsilon_i \sin^2\theta_i \cos 2\phi_i)\right]H_0. \quad (6)$$

Here K_i is the isotropic Knight shift due to the contact interaction with s electrons, whereas the parameters $K_{Z,i}$ and $\varepsilon_i = (K_{Y,i} - K_{X,i})/K_{Z,i}$ are the largest eigenvalue and the asymmetry parameter of the traceless anisotropic Knight-shift tensor that includes the dipolar interaction between the nuclei and the conduction electrons. Since the principal axis systems of both, the anisotropic Knight shift and the EFG tensors are determined by the local symmetry of the nuclear site, we assume that they have the same orientation.

The last term in Eq. (2), $\nu_{\mathrm{exch},i} = (\gamma/2\pi)\Delta H_{\mathrm{exch},i}$, originates from the indirect exchange interaction between the nuclear spins and the d moments of the magnetic Mn atoms via the conduction electrons. The transferred hyperfine field at the position of the ith ^{27}Al nucleus of this RKKY coupling can be written in the original Yosida notation[20] as

$$\Delta H_{\mathrm{exch},i} = \frac{|\langle S_{dz}\rangle|}{\gamma\hbar}\left(\frac{3n}{N}\right)^2 \frac{2\pi}{E_F} A(0)J(0)\sum_j F(2k_F R_{ij}). \quad (7)$$

Here N is the total number of lattice points, n is one-half of the total number of conduction electrons, $J(0)$ is the exchange integral between a conduction electron and the d-core spin of a Mn ion, $A(0)$ is the exchange integral between a conduction electron and the nuclear spin, E_F and k_F represent the Fermi energy and wave vector, respectively, R_{ij} is the distance between the ith nuclear site and the jth magnetic Mn site, and the summation includes all magnetic Mn atoms. The function $F(2k_F R_{ij})$ is the oscillatory function $F(x) = (x\cos x - \sin x)/x^4$, and $\langle S_{dz}\rangle$ represents the thermal average value of the total electronic moment of an Mn ion along the direction of the external field. In a mean-field-type approximation $\langle S_{dz}\rangle$ varies in a Curie-Weiss-type manner as $\langle S_{dz}\rangle \propto H/(T-\theta)$, hence provoking a $1/(T-\theta)$ temperature dependence of the transferred hyperfine field $\Delta H_{\mathrm{exch},i}$. The RKKY shift is the same for all nuclear spin transitions.

Since in the QC lattice the local atomic arrangement is lacking translational periodicity, each nuclear site has its own set of $eq^{(i)}$, η_i, K_i, $K_{Z,i}$, ε_i, $\Delta H_{\mathrm{exch},i}$, θ_i, and ϕ_i parameters. The distribution of these parameters causes an inhomogeneous broadening of the NMR spectrum, whereas their mean values shift its center of gravity.

The large average ^{27}Al quadrupole coupling constants ν_Q of more than 1 MHz found in Al-based icosahedral[12,16,21] QC's as well as surprisingly small Knight shifts of the order of 100–200 ppm in related diamagnetic[22] QC's imply that the first-order quadrupole shift is by far the dominant factor. Therefore the influence of the magnetic interactions on the satellite part of the spectrum is not expected to be observed. Indeed, the satellite part of the ^{27}Al spectrum of $AlPdMn_{7.1}$ does not show any significant changes with temperature. The central line, on the other hand, is quadrupole-perturbed in second-order only, so that other nuclear spin interactions, which broaden the line and shift its center of gravity, become observable. The quadrupolar contribution $\Delta\nu_{1/2,\mathrm{quad}}$ to the total line width $\Delta\nu_{1/2}$ displayed in Fig. 3(a) can be estimated from Eq. (5). Using the value of the quadrupole coupling constant $\nu_Q = 1.31$ MHz, the upper limit of $\Delta\nu_{1/2,\mathrm{quad}}$ is estimated by $\Delta\nu_{1/2,\mathrm{quad}} \leqslant \nu_Q^2/2\nu_0 = 33$ kHz. The total linewidth at room temperature amounts to 55 kHz and we attribute the difference to magnetic broadening. The magnetic part is a sum of the temperature-independent Knight-shift contribution and the RKKY contribution that is characterized by a $1/(T-\theta)$ temperature dependence of both the linewidth and the frequency shift. To extract the relative sizes of these two contributions we first calculated the temperature-dependent parts of $\Delta\nu_{1/2}$ and $\Delta\nu$ by fitting the data of Fig. 3 by $\Delta\nu_{1/2} = \alpha_0 + \alpha_1/(T+26\,\mathrm{K})$ and $\Delta\nu = \delta_0 + \delta_1/(T+26\,\mathrm{K})$, respectively, in the temperature regime $T > 50$ K, where the susceptibility data are compatible with a Curie-Weiss temperature $\theta = -26$ K. The fit procedure (solid lines in Fig. 3) yielded the linewidth parameters $\alpha_0 = (49.9 \pm 0.50)$ kHz and $\alpha_1 = (1950 \pm 40)$ kHz K. The shift parameters are $\delta_0 = (-10.4 \pm 0.25)$ kHz and $\delta_1 = (-1450 \pm 40)$ kHz K for a field B

$=2.35$ T and $\delta_0=(-4.6\pm0.64)$ kHz and $\delta_1=(-771\pm91)$ kHz K for $B=6.3$ T. The parameters α_0 and δ_0 represent the temperature-independent parts of the linewidth and the frequency shift, both of which are the sum of the quadrupolar and the Knight shift contributions. Here we neglect the possible temperature dependence of the quadrupolar contribution due to the EFG tensor changes induced by, e.g., thermal contraction of the lattice. The temperature-independent part of the frequency shift can be written as

$$\delta_0=\frac{a}{H}+bH. \tag{8}$$

Since δ_0 is known at two fields, we can calculate the coefficients a and b. We get $a=-23.7$ kHz T and $b=-0.13$ kHz/T, which yields, for $B=2.35$ T, a second-order quadrupolar shift of $a/H=-10.1$ kHz and a Knight shift $bH=(-0.3\pm0.4)$ kHz. In view of the experimental precision the Knight shift may be considered as vanishingly small and thus negligible. The width $\Delta\nu_{1/2}$ and the frequency shift $\Delta\nu$ of the ^{27}Al spectra shown in Fig. 3 may therefore safely be attributed to the quadrupole and RKKY interactions. In addition to its characteristic $1/(T-\theta)$ temperature dependence, the RKKY interaction is manifested in the NMR spectra also in another way. It produces an asymmetric line shape, as the ^{27}Al nuclei close to Mn moments exhibit large and, e.g., positive RKKY shifts, whereas the shifts of the nuclei in the second coordination shell are smaller and negative, thus creating an asymmetry of the spectrum. The ^{27}Al central lines displayed in Figs. 1 and 2(b) indeed reveal such asymmetries.

In the following we analyze the temperature variation of the RKKY contribution in both the high-temperature regime between 300 and 50 K, and below 50 K, where $\chi(T)$ deviates progressively from the Curie-Weiss-type behavior. In the high-T regime both quantities, $\Delta\nu_{1/2}$ and $\Delta\nu$, exhibit a $1/(T-\theta)$ temperature dependence upon cooling. We assign this variation to the temperature dependence of the exchange field $\Delta H_{\rm exch}$ [Eq. (7)]. The following conclusions for the high-T regime can be made: (i) the ^{27}Al nuclei experience the local magnetic field $\Delta H_{\rm exch}$ of the manganese d moments, transferred via the conduction electrons; (ii) the temperature dependence of $\Delta H_{\rm exch}$ is well described by the Curie-Weiss law and a predominantly antiferromagnetic coupling between the localized d-electron moments of Mn ions, and (iii) the number of moments and their magnitude do not vary with temperature within this temperature regime.

Below 50 K, however, both the linewidth and the frequency shift deviate progressively from the Curie-Weiss prediction. This is especially pronounced below 20 K, where $\Delta\nu_{1/2}$ and $\Delta\nu$ both exhibit a strong and continuous reduction upon cooling. Since, as we have argued above, the intensity of the line that is proportional to the number of resonating ^{27}Al nuclei remains constant in this regime, the local exchange field $\Delta H_{\rm exch}$ at the positions of the ^{27}Al nuclei must be decreasing. The linewidth and the shift at the lowest measured temperature 3 K amount to $\Delta\nu_{1/2}=40$ kHz and $\Delta\nu=-10$ kHz (for $B=2.35$ T). Both values are, within the experimental errors, the same as the pure quadrupolar contributions. We therefore conclude that $\Delta H_{\rm exch}$ shows a tendency to vanish completely. Since $\Delta H_{\rm exch}$ is the field transferred from the Mn moments to the ^{27}Al nuclei by the conduction electrons, there are two possible origins for this to happen. The reduction of $\Delta H_{\rm exch}$ may occur either (i) due to the reduction of the number and/or magnitude of the Mn d moments by some kind of conduction-electron screening of the moments, or (ii) from a reduction of the conduction electron concentration via localization, thus weakening the indirect RKKY interaction. The second possibility would result in a reduction of the Mn transferred field in space around the magnetic ions even in the case that the number and magnitude of the Mn moments remain unchanged. Below we discuss these two possibilities in more detail.

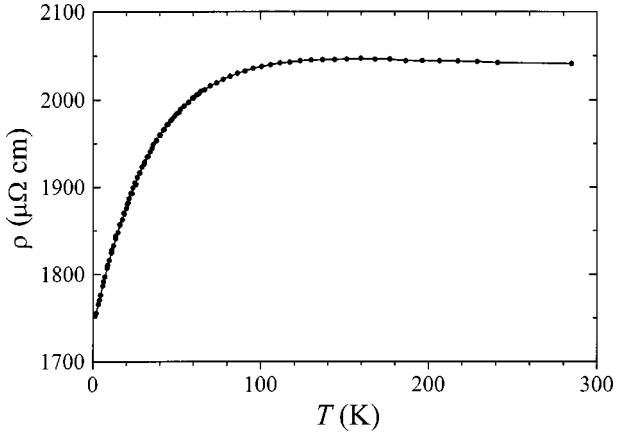

FIG. 5. Temperature-dependent electrical resistivity of the $AlPdMn_{7.1}$ sample in the interval from 300 to 1.6 K.

We first consider the ''screening'' scenario in terms of the Kondo effect. The fraction of magnetic Mn ions at room temperature in $AlPdMn_{7.1}$ is about 1% of all Mn atoms, i.e., a total 0.07% of all atoms in the sample carry magnetic moments. The moments can thus be considered as diluted. In a typical Kondo system (e.g., dilute Cu-Mn or Al-Mn alloys), the NMR manifestation[23] of the Kondo effect at temperatures much higher than the Kondo temperature T_K is the appearance of both a large magnetic broadening and a frequency shift of the spectrum, whose magnitudes vary as $H/(T-\theta)$. Below T_K the broadening and the shift are reduced considerably in size and are temperature independent for $T\ll T_K$. The $AlPdMn_{7.1}$ linewidth and line-shift data shown in Fig. 3 seem to be consistent with that prediction. One of the macroscopic manifestations of the Kondo effect is the appearance of a minimum in the electrical resistivity. The resistance minima were indeed observed at $T\approx4$ K in the i-AlPdMn samples of similar resistivity data[17,24,25] as our $AlPdMn_{7.1}$. However, although our $AlPdMn_{7.1}$ sample exhibits an almost identical resistivity decrease at low temperatures (Fig. 5) as the samples of Refs. 17, 24, and 25, it does not exhibit a resistivity minimum down to the lowest measured temperature of 1.6 K. Another macroscopic manifestation of the Kondo effect is a very small, temperature-independent magnetic susceptibility[26,27] at $T<T_K$, provided the magnetic field is not too strong. The screening conduction electron cloud is, however, highly polarizable, so that

the external magnetic field fulfilling the condition $g\mu_B H \gg k_B T_K$ suppresses the Kondo effect. The magnetic susceptibility data of the $AlPdMn_{7.1}$ are again not consistent with the Kondo prediction. The Kondo susceptibility would, at low temperatures, be reduced with respect to the Curie-Weiss value, so that the inverse susceptibility would lie above the Curie-Weiss line in the $(\chi-\chi_d)^{-1}$ vs T plot. However, the susceptibility data of Fig. 4 lie *below* the Curie-Weiss line, showing a deviation in the opposite (the ''ferromagnetic'') direction from the Kondo prediction. This also excludes the possibility of a partial magnetic-field quenching of the Kondo screening in our experiments, since the susceptibility of a system with a partially suppressed Kondo effect still deviates from the Curie-Weiss line in the Kondo (''antiferromagnetic'') direction. Contrary to the recently claimed[28] Kondo scenario of magnetism in the quasicrystalline AlPdMn, our results on $\rho(T)$ and $\chi(T)$ do not confirm this to be the cause for our observations in the NMR experiments on $AlPdMn_{7.1}$.

As a second possible origin of the temperature-dependent reduction of the Mn transferred field at the ^{27}Al sites we consider a weakening of the RKKY interaction via a reduction of the conduction-electron concentration by localization. The damping of the RKKY interaction oscillations may be significant if the electron mean free path gets shorter than the average distance between the magnetic moments.[9–11] It was shown theoretically[29] that this resistivity-damping of the RKKY interaction results in a considerable narrowing of the NMR spectrum by factors of similar values (of the order 3–5) as those observed in our study. It is generally easy to anticipate the existence of the RKKY resistivity damping in QC's, which mostly exhibit an increasing resistivity upon cooling, associated with a temperature-dependent decreasing electron mean free path due to electron localization. In this scenario the Mn *d* moments do not change in magnitude and number, but the indirect exchange interaction between the moments is reduced, driving the spin system from antiferromagnetically coupled toward uncoupled spins exhibiting genuine Curie-type behavior. The susceptibility deviation from the Curie-Weiss law below 50 K may also be explained in this way. The Curie-Weiss susceptibility of Eq. (1) yields a straight line $(\chi-\chi_d)^{-1}=(T-\theta)/C$ in the plot of Fig. 4, where the slope of the line is determined by the constant C, whereas θ determines the intercept on the abscissa. The reduction of the antiferromagnetic coupling will not affect C but will reduce the absolute value of θ. The $(\chi-\chi_d)^{-1}$ lines with different $|\theta|$ all run in parallel, but those with smaller $|\theta|$ lie lower, intercepting the temperature axis closer to $T=0$. A continuous, temperature-dependent reduction of the Curie-Weiss temperature $|\theta|$ due to the diminishing of the indirect RKKY interaction between the antiferromagnetically coupled Mn spins would then yield a deviation of the susceptibility in the ''ferromagnetic'' direction from the Curie-Weiss prediction, just as is observed for the $AlPdMn_{7.1}$ below 50 K. The reduction of the RKKY coupling at low temperatures thus explains consistently the narrowing of the NMR line and the reduction of its frequency shift, as well as the deviation of the magnetic susceptibility from the Curie-Weiss law. Again, however, we note that the low-temperature features of the electrical resistivity of the $AlPdMn_{7.1}$ are not compatible with a decreasing electron mean free path upon cooling. The resistivity even exhibits a drop of 15% between 100 and 1.6 K, thus indicating an increase of the mean free path. We stress here that the temperature dependence of the $AlPdMn_{7.1}$ resistivity shown in Fig. 5 is still not well understood at present, but it is quite common for *i*-AlPdMn samples with a room-temperature resistivity of about 2000 $\mu\Omega$ cm.

The above analysis shows that neither a Kondo screening nor a mean-free-path damping of the RKKY interaction provides a consistent explanation of the unusual NMR response of $AlPdMn_{7.1}$. The unambiguous experimental result, however, is the indication that the Mn transferred field at the positions of the ^{27}Al nuclei tends to vanish at low temperatures.

V. CONCLUSIONS

The magnetic properties of the *i*-AlPdMn QC family, where only Mn is expected to carry a localized *d* moment, are still not well understood. While samples containing about 9% of manganese per formula unit exhibit spin-glass freezing phenomena at low temperatures, a smaller Mn concentration of 7% yields qualitatively different magnetic properties. Our ^{27}Al NMR experiment on an $AlPdMn_{7.1}$ sample has demonstrated the gradual reduction of the transferred Mn local magnetic field at the positions of the ^{27}Al nuclei at low temperatures. However, a combined analysis of the NMR results and the data on magnetic susceptibility and electrical resistivity does not provide an unambiguous explanation of the unusual magnetism in the quasicrystalline $Al_{72.4}Pd_{20.5}Mn_{7.1}$.

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