Anomalous NMR response of quasicrystalline icosahedral Al$_{72.4}$Pd$_{20.5}$Mn$_{7.1}$ at low temperatures

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We report the observation of an anomalous $^{27}$Al-NMR response of a single grain Al$_{72.4}$Pd$_{20.5}$Mn$_{7.1}$ icosahedral quasicrystal at low temperatures. In an external magnetic field of 6 T and upon decreasing temperature, we observe a sharp 100% increase of the resonance linewidth at 2.5 K. No further changes of the linewidth are observed down to 0.05 K. The linewidth enhancement is accompanied by a small but distinct increase of the spin-lattice relaxation rate $T_1^{-1}$ and by a maximum of the spin-spin relaxation time $T_2(T)$. All these anomalies are absent in external fields of 2.5 T and below. Our observations indicate unusual variations in the stability of isolated magnetic moments in a quasiperiodic metallic environment.

Various physical properties of icosahedral quasicrystals of Al-Pd-Mn alloys have been studied in recent years. Especially intriguing are their magnetic properties [1–3]. For example, from data of the magnetic susceptibility and the specific heat, as well as from the results of calculations of the electronic structure, [1,4,5] it has been inferred that in these materials only a small fraction, of the order of 1%, of Mn ions carry a magnetic moment. The coexistence of magnetic and nonmagnetic Mn sites in Al-rich quasicrystals has also been discussed for Al-Pd-Mn quasicrystals with slightly varying chemical composition. [6–8] The formation or the absence of ionic magnetic moments at the Mn sites in Al-Pd-Mn quasicrystals has first been attributed to differences in the local chemical environment of the Mn ions. In particular it was claimed [4] that a weak Al-p-Mn-d hybridization leads to the formation of well localized and rather large Mn moments. More recently, however, it has been suggested [5] that the local environment of the Mn ions alone cannot explain why only few Mn ions carry a magnetic moment and that also Mn-Mn interactions over large distances ought to be taken into account.

Previous $^{27}$Al NMR experiments [3] on a single grain quasicrystal with a composition of Al$_{72.4}$Pd$_{20.5}$Mn$_{7.1}$ have shown that the small number of magnetic Mn ions decreases even further with decreasing temperature below approximately 20 K. This unusual behavior in this temperature range was revealed by a reduction of the NMR linewidth with decreasing temperatures, as well as by indicative features of the temperature dependence of the magnetic susceptibility $\chi(T)$. So far, the cause for these observations is not clear.

In this work we present experimental evidence for additional anomalies in the temperature dependences of the NMR spectra and the spin lattice relaxation rate $T_1^{-1}$ of an icosahedral Al$_{72.4}$Pd$_{20.5}$Mn$_{7.1}$ quasicrystal. In external magnetic fields of the order of 6 T and with decreasing temperature we observe drastic changes in the temperature dependences of both the $^{27}$Al- and the $^{55}$Mn-NMR linewidth at $T_b = 2.5$ K, accompanied by distinct variations in the temperature dependences of both the spin-lattice and the spin-spin relaxation rates $T_1^{-1}(T)$ and $T_2^{-1}(T)$. None of these anomalies is observed in fields of the order of 2.5 T or smaller.

The investigated sample was a single-grain piece of quasicrystalline material with a nominal composition of Al$_{72.4}$Pd$_{20.5}$Mn$_{7.1}$, grown by the Czochralski technique and annealed at 850 °C. Its chemical and structural quality has been discussed in ref. 9. The same sample, previously used to perform measurements of $^{27}$Al-NMR spectra at higher temperatures [3], has also been characterized by measurements of the magnetic susceptibility and the electrical conductivity between 1.5 and 300 K. In all our NMR experiments, standard spin-echo techniques have been employed.

![FIG. 1. Central part of the $^{27}$Al-NMR spectra of Al$_{72.4}$Pd$_{20.5}$Mn$_{7.1}$ icosahedral quasicrystal measured at 71.33 MHz and three temperatures. The solid lines represent the best fits to the data using a Lorentzian-type function with a degree of asymmetry built into it.](image-url)
The well defined peaks in the spectra represent the central Zeeman transition \((1/2 \leftrightarrow -1/2)\) of the Al nuclei. The wings of the spectrum, \(i.e.,\) the \(\pm1/2 \leftrightarrow \pm3/2\) and \(\pm3/2 \leftrightarrow \pm5/2\) transitions caused by the electric quadrupolar perturbation of the Al nuclear Zeeman levels \((I = 5/2)\) are distributed over a broad range of resonant fields, a feature that seems to be generic for quasicrystals\(^{10}\). The full NMR spectrum of our material is shown in ref. 3, revealing that the temperature dependence of the wings does not exhibit any anomalies at low temperatures. Thus the sudden increase of the NMR linewidth observed at 2.5 K and shown in Fig. 2 is of magnetic, and not of electric quadrupolar origin. Hence, the following analysis and discussion consider the central transition.

Two sharp features can clearly be distinguished in the temperature dependence of the \(^{27}\text{Al}\)-NMR linewidth \(\Delta\) (FWHM) measured at 67 MHz (see Fig. 2). These are, a discontinuity in \(\Delta\) and a break in its slope at \(T_b = 2.5\) K and \(T_a \approx 15\) K, respectively. As may also be seen in the same figure, \(\Delta\) decreases substantially with decreasing temperature between \(T_a\) and \(T_b\). This loss of linewidth, already reported in ref. 3, is recovered almost discontinuously at \(T_b\) and \(\Delta(T)\) is approximately constant below that temperature. This particular behavior is observed at Larmor frequencies of 67.00 and 45.75 MHz, but is absent in much lower magnetic fields. This is emphasized in Fig. 2, where \(\Delta(T)\) of the central \(^{27}\text{Al}\) Zeeman transition for spectra measured at 67.00 and 26.00 MHz, corresponding to applied magnetic fields of 6.4 and 2.5 T, respectively, is displayed. While \(\Delta(T)\) is approximately the same for both cases between \(T_a\) and \(T_b\), no discontinuous enhancement of \(\Delta\) is manifest in the data set measured at 26 MHz.

In Fig. 3, we show three examples of \(^{55}\text{Mn}\)-NMR spectra, recorded at a fixed frequency of 71.33 MHz and at temperatures of 0.48, 3.0 and 20 K. The central transition \((1/2 \leftrightarrow -1/2)\) of the \(^{55}\text{Mn}\) nuclei is centered at approximately 6.79 T. As the \(^{27}\text{Al}\) nuclei, also the \(^{55}\text{Mn}\) nuclei carry a spin of \(I = 5/2\) and thus exhibit a relatively large electric-quadrupole moment. Also here, the quadrupolar wings are expected to be widely spread out and indeed, they cannot be resolved in our experiments. Considering the small lineshift, of the order of \(-0.3\%\), as well as the moderate linewidth monitored in the \(^{55}\text{Mn}\)-NMR central transition, we conclude that the observed Mn-NMR signal originates from Mn nuclei of non magnetic ions. Because of the expected generation of large hyperfine fields the resonance of the nuclei of magnetic Mn ions is assumed to be outside our observation range. By comparing the integrated intensities of the recorded central lines for \(^{27}\text{Al}\) and \(^{55}\text{Mn}\) nuclei, and taking into account the differences in the intrinsic NMR intensities for \(^{27}\text{Al}\) and \(^{55}\text{Mn}\), we conclude that at most a few percent of the Mn ions carry a magnetic moment.

![FIG. 2. \(^{27}\text{Al}\)-NMR linewidth \(\Delta\) as a function of temperature for data measured at 26.00 and 67.00 MHz. Sharp features are observed in \(\Delta(T)\) for the data measured at 67 MHz at \(T_a = 15\) K and \(T_b = 2.5\) K. The solid lines are guides to the eye](image)

![FIG. 3. Central transition of the \(^{55}\text{Mn}\)-NMR spectra of \(\text{Al}_{72.4}\text{Pd}_{20.5}\text{Mn}_{7.1}\) icosahedral quasicrystal measured at 71.33 MHz and three temperatures. The solid lines represent the best fits to the data using a Lorentzian-type function with a degree of asymmetry built into it.](image)
as a function of the time delay $\tau$ between the two pulses of a $\pi/2 - \tau - \pi$ spin-echo sequence. The effective rate $T_2^{-1}$ was then calculated via $T_2^{-1} = T_2^{-1} - T_1^{-1}$. The spin-lattice relaxation rate $T_1^{-1}$ was measured separately and was found to be much smaller than $T_2^{-1}$ at all temperatures covered in our experiments. The results for $T_2^{-1}(T)$, evaluated for the $^{27}$Al-NMR central transition at the Larmor frequency of 67.00 MHz, are displayed in Fig. 4. We note the gradual increase of $T_2^{-1}$ with decreasing temperatures below $T_a$ and, again near $T_b$, its rather abrupt reduction by more than a factor of five. This overall behavior is to be compared with previous observations involving metals with atoms containing unfilled $3d$-electron shells, such as Mn, where one often finds, with decreasing $T$, a progressive increase of the NMR linewidth, an increase of $(T_1T)^{-1}$ and, if any, a reduction of $T_2^{-1}$. Both the reduction of the NMR linewidth and the increase of $T_2^{-1}$ with decreasing $T$ below $T_a$ are thus unexpected, but they seem to be related to each other. Similarly, the sharp changes in the $FWHM$ and in $T_2^{-1}$ and to a lesser extent in $(T_1T)^{-1}$, observed at $T_b$, undoubtedly reflect a common cause.

In attempting a further characterization of the anomalous NMR response of Al$_{72}$Pd$_{20.5}$Mn$_{7.1}$ at low temperatures, we have measured the temperature dependence of the NMR spin-lattice relaxation rate $T_1^{-1}$ under various experimental conditions. Contrary to what has been suggested previously [1] we found no evidence for any appreciable contribution to $T_1^{-1}$ from quadrupolar relaxation. In Fig. 4 we display $(T_1T)^{-1}$ as a function of $T$, with $T_1$ measured at the central transition of the $^{27}$Al nuclei, for two different applied magnetic fields of 1.147 and 6.054 T, corresponding to Larmor frequencies of 12.70 and 67.00 MHz, respectively.

![Figure 4](image1)

**FIG. 4.** Spin-spin relaxation rate $T_2^{-1}$ as a function of temperature measured at the $^{27}$Al-NMR central transition at 67 MHz. Note the rapid increase of $T_2^{-1}$ with decreasing $T$ below $T_a$ and the distinct maximum at $T_b$. The dotted line is a guide to the eye.

Considering the relaxation data measured at 6.054 T, we note that below $T_b$, $(T_1T)^{-1}$ gradually increases with decreasing temperatures. This is not unusual for quasicrystals. For example, a qualitatively similar behavior, i.e., an increase of $(T_1T)^{-1}$ by more than an order of magnitude below approximately 20 K, has previously been reported for a nonmagnetic Al$_{70}$Re$_{8.6}$Pd$_{21.4}$ icosahedral quasicrystal [2] and very recently, a similar behavior has been observed in $T_1^{-1}(T)$ of Al$_{70}$Re$_{10}$Pd$_{20}$ [3]. In the former case it has been suggested that this might reflect the critical nature of the itinerant-electron states whose existence in quasicrystals is presently a matter of debate [4]. More recently it has been suggested [13] that paramagnetic impurities, inadvertently introduced during the synthesis of the material, may in general be the cause of the anomalous low temperature spin-lattice relaxation observed in quasicrystals. However, this would lead to a strongly field-dependent spin-lattice relaxation rate $T_1^{-1}(T)$, contrary to previous experimental observations [12] and therefore, this scenario cannot be regarded as being valid in all cases, indicating that the low-temperature behavior of $T_1^{-1}(T)$ of quasicrystals remains an interesting unsolved problem.

In our case, however, a small number of magnetic Mn ions has to be considered. The $\chi(T)$ data, exhibiting a Curie-Weiss-type feature above 20 K, reveals a small paramagnetic Curie temperature and an effective magnetic moment corresponding to a concentration $c \approx 1\%$ of magnetic Mn$^{3+}$ ions ($S = 2, L = 0$). Consequently it seems appropriate to consider the remaining magnetic Mn$^{3+}$ ions as isolated magnetic moments, i.e., “paramagnetic impurities”. For this case the temperature and field dependences of the nuclear relaxation rate $(T_1^{\text{imp}})^{-1}$, at temperatures where the random fluctuations of the impurity moments are not correlated, is given by [15,17].

![Figure 5](image2)

**FIG. 5.** $(T_1T)^{-1}$ as a function of temperature measured at the $^{27}$Al-NMR centraltransition at 67.00 and 12.70 MHz. Above $T_a = 15$ K, $T_1^{-1}$ may be regarded as caused by the conduction electrons and isolated Mn magnetic moments (solid lines). The latter contribution, however, turns into a power law below $T_b = 2.5$ K (broken lines).
\[
\frac{1}{T_1^{imp}} \propto c \cdot \langle S^z \rangle \cdot \frac{\tau}{H} \left(1 + (\omega \tau)^2\right)^{-1},
\]

where \( \tau \) is a time scale characterizing the spectrum of fluctuations of the impurity (correlation time) and \( \langle S^z \rangle \) is the average \( z \)-component of the impurity spins induced by \( H \). For simplicity we assume that \( \langle S^z \rangle \) has a Curie-type temperature dependence \([5]\). The angular Larmor frequency \( \omega \propto H \). Since our quasicrystalline material is metallic, an additional Korringa-type contribution to the spin-lattice relaxation rate via the conduction electrons, \( (T_1^{ce})^{-1} \), is expected \([10]\). In total,

\[
(T_1 T)^{-1} = (T_1^{ce} T)^{-1} + (T_1^{imp} T)^{-1}.
\]

Indeed the experimental data above \( T_a \) are fairly well represented by invoking the above mentioned interpretation. The solid lines in Fig. 5 are based on Eq. 2, both with the same value of \( (T_1^{ce} T)^{-1} \approx 0.019 \text{ K}^{-1} \text{ s}^{-1} \), indicating that the relaxation via conduction electrons is field-independent. This relaxation rate is very close to that reported in ref. 20 for Al\(_{23}\)Pd\(_{15}\)Re\(_{10}\) but by nearly a factor of 3 lower than the corresponding rate observed in nonmagnetic Al\(_{70}\)Pd\(_{20}\)Re\(_{10}\) \([5]\) and Al\(_{70}\)Re\(_{8.6}\)Pd\(_{21.4}\) \([21]\). This is rather surprising because the electrical conductivities \( \sigma(T) \) of the Re alloys are, respectively, between one and two orders of magnitude lower than \( \sigma(T) \) of our Al-Mn-Pd quasicrystal \([3,21]\). Thus this observation might indicate that the electrical transport in quasicrystals is not simply dictated by the number of itinerant charge carriers, but is dominated by scattering processes that are not well understood.

Because of the factor \((1 + \omega^2 \tau^2)^{-1}\) in Eq. (1), the magnitude of the second term in Eq. (2), due to the relaxation via impurity spins, is influenced by the strength of the external field. Our fits, considering the respective field values and assuming a temperature - and field - independent \([22]\) correlation time \( \tau \) in this temperature range, imply a very large value of \( \tau = 7 \cdot 10^{-9} \text{ s}^{-1} \). This is orders of magnitude larger than those expected for dilute paramagnetic impurities in metals, such as Gd impurities in LaAl\(_2\) \([22]\). Since there is no obvious reason for an extremely weak coupling between the moments and the conduction electrons, the correlation time \( \tau \) may be large because of the proximity of a magnetic phase transition at temperatures of the order of \( T_a \), slowing down the moment fluctuations.

We note that the salient features in the \( T \) dependence of \( T_1^{-1} \) are definitely field dependent below \( T_a \). The low field data for \((T_1 T)^{-1}\) exhibit a clear break in the slope \( \partial(T_1 T)^{-1}/\partial T \) at or very near \( T_a \) which may, in the most straightforward way, be interpreted as a sudden variation of \( T_1 \), due to a change in the interaction between fluctuating impurities.

The high field data differs in the sense that, if at all, the break in the slope of \((T_1 T)^{-1}(T)\) at or very near \( T_a \) is barely visible, but instead a discontinuity in \((T_1 T)^{-1}\) at \( T_b \), concomitant with the discontinuous line width enhancement, is observed. Both in high and low fields, the linewidths are nearly temperature independent below \( T_b \), but the relaxation rates \( T_1^{-1} \), vary as \( (T_1 T)^{-1} \approx (T_1^{ce} T)^{-1} + C(H) \cdot T^{-0.35} \), represented by the broken lines in Fig. 5. Here \( C(H) \approx 0.018 \) and \( 0.065 \text{ K}^{-0.65} \text{ s}^{-1} \) for the frequencies of 67 and 12.7 MHz, respectively. This allows that the contribution of the conduction electrons to the spin-lattice relaxation rate is not altered very much at low temperatures, as suggested by the small changes of \( \rho(T) \) observed in our sample below 15 K \([3]\). In any case, the temperature and field dependences of \( \Delta \) and \( T_1^{-1} \) below \( T_a \) are very unusual. Although, our sample seems to be close to some kind of magnetic instability above \( T_a \), our observations for the low temperature regime \( T \leq 15 \text{ K} \) cannot be reconciled with expectations, neither for non-magnetic hosts containing magnetic impurities, nor for spin glasses or magnetically ordered systems.

In conclusion we report here the observation of unusual anomalies in the NMR response of an icosahedral AlPdMn quasicrystal, which to our knowledge have not been reported to occur in periodic crystals. The low-temperature features of Al\(_{72}\)Pd\(_{20}\)Mn\(_{7.1}\) observed in this work seem to indicate unusual variations in the stability of transition metal (Mn) ionic moments in a non-periodic metallic matrix at different temperatures. At present we have no convincing explanation for the observed phenomena (see also reference 3), but in view of the covered temperature regimes, they must be related to rather low characteristic energies.

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