Low-Temperature Nuclear Magnetic Resonance Studies of an $Al_{70}Re_{8.6}Pd_{21.4}$ Icosahedral Quasicrystal

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We report the results of a ^{27}Al nuclear magnetic resonance study of icosahedral quasicrystalline $Al_{70}Re_{8.6}Pd_{21.4}$ at temperatures between 0.04 and 300 K and in magnetic fields between 1.5 and 7 T. At very low temperatures we have found that the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}(T)$ shows new and unexpected features which we associate with a gradual real-space localization of the itinerant charge carriers. Above 20 K, $T_1^{-1}(T)$ contains both a linear- and a cubic-in-T term, previously observed for other quasicrystals. [S0031-9007(97)04282-8]

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In recent years a great deal of experimental and theoretical efforts have been devoted to the understanding of the unusual structural and physical properties [1] of the so-called quasicrystals, which are solids with highly ordered but nonperiodic structures. In particular, icosahedral quasicrystals such as those based on Al, Mn, and Pd (Al-Mn-Pd) [2] or Al, Re, and Pd (Al-Re-Pd) [3], display long-range quasiperiodic order in three dimensions, and can be synthesized with high structural perfection.

A prominent physical property of Al-Re-Pd quasicrystals is their extremely low electrical conductivity, albeit with significant temperature dependencies [4–6]. The low-temperature specific heat of these materials contains a small contribution varying linearly with temperature, adding evidence that Al-Re-Pd quasicrystals are generally rather poor metals [5–8]. This interpretation got further support from optical properties [6,8] and from the results of tunneling [9] experiments. Previous NMR results of quasicrystals [10–13] have mainly been interpreted as confirming the conjecture of a pseudo gap in the electronic excitation spectrum at the Fermi energy for some quasicrystals and their periodically structured approximants. In addition, a distribution of environments on the atomic scale for these materials has been inferred from those studies.

Here we report the first NMR results between 0.04 and 300 K for a high-quality icosahedral quasicrystalline sample of the Al-Re-Pd family, well characterized by measurements of structural, thermal, and transport properties [6,7]. At very low temperatures we have found that the ^{27}Al-NMR response of icosahedral $Al_{70}Re_{8.6}Pd_{21.4}$ shows new and unexpected features that may, for the first time, give direct evidence for critical electronic states in quasicrystals.

For our ^{27}Al-NMR experiments we used standard spin-echo techniques in external magnetic fields between 1.5 and 7 T and temperatures between 0.04 and 300 K. The ^{27}Al-NMR spectra were measured both at a fixed applied magnetic field by monitoring the spin echo signal at a given frequency and varying stepwise the frequency, and by varying stepwise the applied magnetic field at a fixed frequency. The spin-lattice relaxation rate was measured by destroying the nuclear magnetization with either a short or a long comb of rf pulses and observing the nuclear magnetization recovery towards thermal equilibrium. The different irradiation conditions, i.e., short or long irradiation, produce different types of recovery for the nuclear magnetization, but both cases yield similar values for the spin-lattice relaxation rate. Because of the broad wings of the ^{27}Al-NMR spectra, we irradiated only the central peak corresponding to the $+\frac{1}{2} \leftrightarrow \frac{1}{2}$ nuclear Zeeman transition. We have performed several tests to eliminate artifacts extraneous to the intrinsic relaxation, such as rf heating of the sample. Below 4 K, our sample was immersed in the liquid mixture of a ^{3}He-^{4}He dilution refrigerator, and above 4 K it was placed in contact with flowing He gas. Because of the unusually low electrical conductivity of $Al_{70}Re_{8.6}Pd_{21.4}$ we have been able to perform our measurements on a bulk polygrained sample, thus avoiding the possible introduction of random strains in the structure, which sometimes occurs during the powdering process and could alter the NMR response.

In Fig. 1 we display an example of an ^{27}Al-NMR spectrum for $Al_{70}Re_{8.6}Pd_{21.4}$, measured at $T = 1.07$ K and a fixed frequency of 16.667 MHz. The sharp peak in the center of the spectrum represents the central $(+\frac{1}{2} \leftrightarrow \frac{1}{2})$ nuclear Zeeman transition of Al and the broad background is caused by the quadrupolar perturbation of the Zeeman levels. Measurements near the center of the spectrum with higher resolution (see inset of Fig. 1) were made by changing stepwise the frequency at a fixed field. The solid lines in the figure and in the inset represent best fits to the data using a model which assumes a broad distribution of electric-field gradients at the Al sites. The model also considers a small isotropic NMR line shift K as an additional fitting parameter, which here is identified as an average Knight shift. Our model yielded consistent results for the Knight shift and field gradients at the Al sites for all spectra measured at different fields and temperatures between 0.04 and 300 K.

Because our analysis showed that the broad background displayed in Fig. 1 is not influenced by changing the magnetic field, it is not due to a distribution of susceptibilities.

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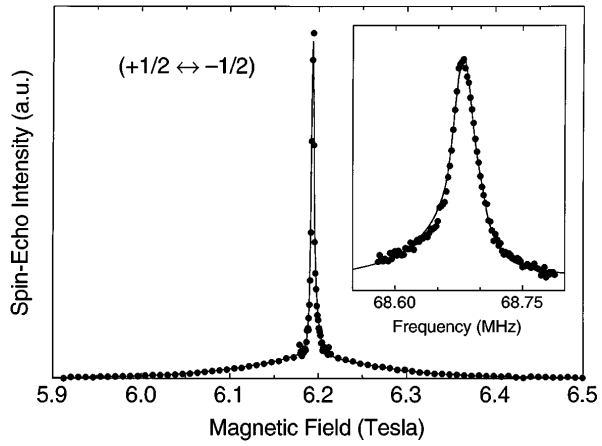

FIG. 1. ^{27}Al-NMR spectrum for $Al_{70}Re_{8.6}Pd_{21.4}$ measured at a temperature of 1.07 K and a fixed frequency of 16.667 MHz. The solid line represents a fit to the data using a model that assumes a distribution of field gradients at the Al sites. The inset shows data close to the resonance in a fixed magnetic field of 6.19 T and at 1.06 K.

The ^{27}Al-NMR line shift is positive and small, K is of the order of 120 ± 30 ppm and is temperature independent below 100 K. This result implies a metallic type of electronic state for $Al_{70}Re_{8.6}Pd_{21.4}$, albeit with a very low density of electronic states (DOS) at the Fermi energy E_F. The error bars estimated for our Knight-shift data do not allow us to establish whether K has a weak, if any, temperature dependence above 100 K.

In Fig. 2 we show the temperature dependence of the spin lattice relaxation rate T_1^{-1} for $Al_{70}Re_{8.6}Pd_{21.4}$ between 18 and 300 K. The inset gives an example of the nuclear magnetization recovery used to extract the spin-lattice relaxation rate T_1^{-1}. This particular data set was measured at 285 K in an applied field of 5.7 T, employing a short comb of rf pulses to irradiate the central line of the NMR spectrum. The broken line represents a two-parameter fit to the data, appropriate for the conditions of this measurement with the two fitting parameters being a single spin-lattice relaxation time T_1 and an overall scaling factor. Even better fits to the data are obtained by assuming a distribution of T_1's, which might be expected here. However, since this type of analysis does not change qualitatively our main results, we assume for simplicity a single T_1.

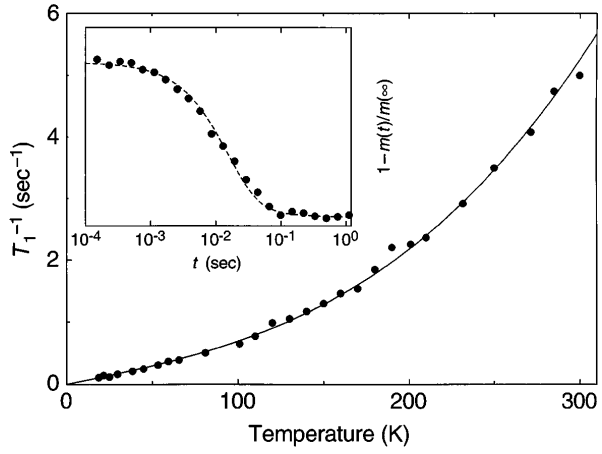

FIG. 2. $T_1^{-1}(T)$ for $Al_{70}Re_{8.6}Pd_{21.4}$. The solid line represents a fit to the data using Eq. (1). The inset shows an example of the nuclear magnetization recovery, measured at 285 K and in a magnetic field of 5.7 T. A fit to the data for the case of a single T_1 (broken line) is shown.

The solid line in Fig. 2 represents a fit to the data of the form

$$T_1^{-1}(T) = aT + bT^3, \tag{1}$$

with $a = 0.56 \times 10^{-2}\ \mathrm{K^{-1}\,s^{-1}}$ and $b = 1.3 \times 10^{-7}\ \mathrm{K^{-3}\,s^{-1}}$. The first term, typical for simple metals, dominates the spin-lattice relaxation below 100 K. In our case, a is very small, corresponding to a relaxation rate roughly 2 orders of magnitude smaller than for Al metal. Small relaxation rates varying linearly with temperature have previously been observed for other quasicrystals [10,11,13]. In Fig. 3 the collapse of the data onto a single curve by plotting the nuclear magnetization recovery as a function of tT, the time-delay multiplied by the corresponding temperature, demonstrates that $T_1^{-1}T$ is approximately constant between 18 and 80 K. The second term on the right hand side of Eq. (1) is more difficult to interpret, but it has also previously been observed for other quasicrystals and has been associated with a pseudogap in the DOS at E_F [11]. In general, the existence of a pseudogap at or near E_F implies an increase of the Knight shift with increasing temperatures which is not corroborated by the results of our experiments. We have stated above that K has, if any, only a weak temperature dependence. More experiments above 300 K would be needed to resolve this issue.

In Fig. 4 we display a summary of our results for T_1^{-1} for $Al_{70}Re_{8.6}Pd_{21.4}$ below 80 K. The data below 20 K

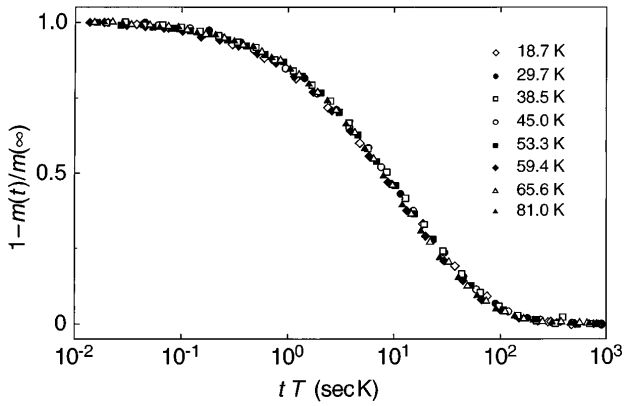

FIG. 3. Normalized nuclear magnetization recovery data for various temperatures T as a function of tT. The data collapse onto a single curve implies that T_1T is constant between 20 and 100 K.

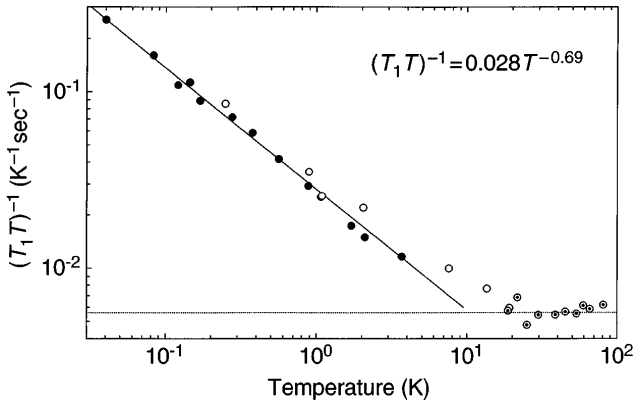

FIG. 4. $(T_1T)^{-1}(T)$ below 80 K. Data above 20 K were measured at 5.7 T and below 20 K at 1.5 T (empty circles) and at 6.19 T (filled circles). The solid line represents a power-law fit. The dotted line indicates the Korringa law valid above 20 K.

represented by filled circles (1.5 T) and empty circles (6.19 T) imply that the measured relaxation rates are field independent. The solid line represents a fit to the data using a function of the form

$$(T_1T)^{-1} = \alpha T^{-0.69}, \tag{2}$$

and the dotted line is compatible with the constant $(T_1T)^{-1}$ value established above. The data obviously signal a dramatic increase in the strength of the nuclear relaxation mechanism, as measured by $(T_1T)^{-1}$, which for metallic systems is generally associated with a rapid slowing down of electronic fluctuations. The most common cases involve critical phenomena preceding a cooperative magnetic phase transition or the onset of spin-freezing in spin-glass systems. There is absolutely no evidence for this from thermal and transport properties of our material, down to temperatures in the millikelvin region [6,7]. Electronic slowing-down processes are also found in strongly correlated electron systems, such as heavy-electron metals. The formation of the heavy-electron ground state is accompanied by a large enhancement of the spin-lattice relaxation rates at low temperatures [14]. Again, there is no evidence for strong correlations among the itinerant electrons of $Al_{70}Re_{8.6}Pd_{21.4}$.

As the most probable scenario, we consider the onset of a metal-insulator transition from the metallic side, as observed for metal-ammonia or alkali metal-alkali halide solutions [15], and for doped semiconductors [16]. In the insulating regime the electronic fluctuations occur independently, whereas in the metallic state the restriction imposed by the Fermi statistics results in a spreading of the spectra of electronic fluctuations over a very large frequency range. On approaching the metal insulator transition from the metallic side the Fermi statistics loses its dominance and the spectrum of electronic fluctuations shifts towards lower frequencies, resulting in an increase of $(T_1T)^{-1}$. Thus our NMR results suggest some gradual real-space localization of the itinerant electrons in $Al_{70}Re_{8.6}Pd_{21.4}$ at low temperatures.

It is difficult to identify with certainty the mechanisms responsible for the spin-lattice relaxation in Al-Re-Pd at low temperatures because details of the characteristics of the electronic states are presently unknown. We notice, however, that the transport properties of Al-Re-Pd quasicrystals are very sensitive to the concentration of Re atoms in the chemical composition [6]. Hence it seems reasonable to assume that the electronic states for Al-Re-Pd result from strong hybridization of extended Al p and d wave functions with Re d orbitals [17]. It may then be expected, at least at low temperatures, that spin-flip scattering of the conduction electrons at the nonmagnetic Re ions would limit the lifetime of a spin orientation for the conduction electrons and, therefore, would contribute to the spin-lattice relaxation rate. A perturbation treatment of the spin-orbit interaction V_{so} responsible for the spin-flip scattering yields [18]

$$\frac{1}{T_1} \propto c|\langle\beta|V_{\mathrm{so}}|\beta\rangle_{\mathrm{FS}}|^2\rho(E_F), \tag{3}$$

where b are the exact one-electron states of electrons moving in the resulting electric field of the lattice and the impurity (Re ion), but neglecting the spin orbit interaction, $\rho(E_F)$ is the DOS at the Fermi energy, c is the concentration of Re ions and the matrix element is averaged over the Fermi surface. A large spin-orbit interaction is characteristic of high-Z nuclei such as Re and, furthermore, their contribution to the relaxation rate is more important if there is a substantial valence difference between the host (Al, Pd) and the impurity (Re) ions. It is therefore conceivable that electronic localization at the Re sites would favor an enhancement of the spin-lattice relaxation rate.

This tendency of electron localization in real space brings into consideration the concept of critical electronic states [19], inherent to quasiperiodic solids. These states are neither extended nor localized and at high temperatures thermal excitations are expected to mask their difference from truly extended states. It is conceivable that they exhibit their true critical character at only low temperatures. These critical states may best be characterized by an increasing degree of electronic localization with decreasing temperature, never quite arriving at an insulating state. This description matches qualitatively the experimental results for the temperature dependence of dynamical properties of $Al_{70}Re_{8.6}Pd_{21.4}$ such as the spin-lattice relaxation rate T_1^{-1}. The Knight shift data imply that the average density of electronic states at the Al sites does not change appreciably with temperature, which may be expected if the critical states at the Re sites extend over several lattice sites [20]. In any case the NMR linewidth of $Al_{70}Re_{8.6}Pd_{21.4}$ is dominated by a distribution of quadrupolar couplings and therefore is not very sensitive to small changes in the distribution of Knight shifts. We emphasize that the above discussion of critical states is meant to suggest a possible

scenario that is consistent with our NMR results. Further experiments probing the nature of electronic states in quasicrystals would, of course, be helpful especially because the low temperature electrical-transport properties of these materials are subject to considerable variations.

Finally, we mention that a similarly unusual type of NMR relaxation has recently been found in proton glasses. The unusual behavior of $T_1^{-1}(T)$ has been associated with quadrupolar relaxation caused by tunneling states [21]. At very low temperatures this is expected to yield a temperature independent relaxation, close to what we observe. We cannot yet completely rule out such a scenario, because tunneling states in the lattice system of this material have been inferred from measurements of the thermal conductivity via lattice excitations [7]. At present, however, we have no evidence for quadrupolar-driven relaxation that might result from tunneling states. A future search for their signature in the NMR spectra, using 2D NMR techniques, is envisaged.

The main result of our study is the observation of an unexpected increase of $(T_1T)^{-1}$ related with nuclear relaxation in $Al_{70}Re_{8.6}Pd_{21.4}$ with decreasing temperature below 20 K. This increase seems to follow a power law with no sign of saturation down to temperatures of the order of 0.05 K. We suggest that this phenomenon provides evidence for critical electronic states in $Al_{70}Re_{8.6}Pd_{21.4}$ icosahedral quasicrystals.

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