Atomic Motion in Quasicrystalline $Al_{70}Re_{8.6}Pd_{21.4}$: A Two-Dimensional Exchange NMR Study

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^{27}Al 2D exchange NMR experiments on an icosahedral $Al_{70}Re_{8.6}Pd_{21.4}$ quasicrystal have detected slow atomic motions in the sub-kHz range at temperatures between 0.16 and 130 K. The observed motion is limited in space and can be associated with local phason fluctuations at very low energies, involving quantum tunneling at very low temperatures. It may thus be regarded as an atomic motion acting as a precursor to bulk self-diffusion. [S0031-9007(98)07456-0]

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The dynamics of quasicrystalline structures, exhibiting perfect long range order but involving symmetries incompatible with the periodic translational order of common crystalline lattices, is one of the topics of condensed matter physics in need for various clarifications. Of the Goldstone modes found for quasiperiodic lattices, three are ordinary sound waves and the others are phason modes [1]. In contrast to incommensurate systems, the phason modes in quasicrystals (QC's) may not be regarded as collective long-wavelength propagating modes because the motion of atoms occurs as discontinuous jumps. The phason dynamics is one of the key issues in the physics of QC's related to phase transitions [2], low temperature lattice excitations [3], structural models [4], the stability of the structure in the random tiling model [5], and diffusion [6]. Quenched phason strains were identified many times via, depending on the strain distribution, the displacement or the broadening of Bragg peaks in scattering experiments, but the evidence for phason motion is still scarce. Neutron scattering experiments revealed details of phason motion at temperatures above 800 K [7,8]. It is also believed that phason flips provide a mechanism for improving the perfectness of the QC structure via annealing quenched phason strains just below the decomposition temperature, i.e., at temperatures typically exceeding 850 K.

We present a ^{27}Al two-dimensional (2D) exchange NMR study of the structural dynamics of icosahedral $Al_{70}Re_{8.6}Pd_{21.4}$ (Al-Re-Pd) in the temperature interval between 0.16 and 130 K. The results imply slow incoherent spatial motions of atoms in the inhomogeneous electric field gradient over interatomic distances with frequencies in the 0.1–100 Hz range. Our results are, to the best of our knowledge, the first clear manifestation of unusual phason dynamics in QC's at low and very low temperatures. The motion persists at very low temperatures and is thermally activated above 1 K. It occurs on a much faster time scale than what is extrapolated from bulk diffusion experiments above 520 K (see below) and is, unlike bulk diffusion processes, confined in space.

In periodic crystals the bulk diffusion results mainly from the presence of lattice vacancies. The diffusion is thermally activated with a total activation energy that includes the energy of a vacancy creation and the activation energy of an atomic jump. For periodic crystals with simple lattices the total activation energy was found to be of the order of 2–3 eV [9]. Kalugin and Katz [6] predicted that in QC's, contrary to periodic crystals, no vacancies are necessary for bulk diffusion. They argued that, in regular QC's, phason flips can lead to unbounded motion of atoms and, consequently, to diffusion. This mechanism depends on two characteristic energies, i.e., the activation energy of an atomic jump and the energy of a single violation of the matching rules, i.e., constraints on local configurations that completely determine the global structure [10] by local rearrangements of atoms. The activation energy of an atomic jump is expected to be lower than in periodic crystals, mainly because the distances of phason-related atomic jumps in QC's are definitely shorter than in periodic crystals and because of more shallow potentials around some of the atomic positions. The energy cost of a single violation of the matching rules relates to the disarrangements of atoms in the second coordination shell and therefore is not expected to be high either.

The conjecture of Kalugin and Katz of self-diffusion in QC's based on phason fluctuations has been confirmed by Monte Carlo simulations of phason dynamics for an ideal quasiperiodic tiling and for random tilings [11,12]. In both cases this anomalous atomic motion is described by a diffusion constant of the form

$$D(T) = D_0 \exp(-\epsilon/T), \tag{1}$$

where ϵ is, in general, a temperature-dependent activation energy. At very low temperatures $D(T)$ is expected to saturate at a nonzero value due to remanent atomic hopping requiring extremely low energies [11].

These processes with low activation energies are expected to dominate the diffusion in QC's at low temperatures. The conventional vacancy diffusion in QC's, because of its higher activation energy, is expected to be of significance only at high temperatures. Indeed, the use

of radiotracer methods involving ^{54}Mn and ^{59}Fe in Al-Pd-Mn [13,14] and Al-Cu-Fe [15] icosahedral phases has shown that above 700 K the quasicrystalline diffusion is not significantly different from the related crystalline approximant materials, for which a vacancy-mediated diffusion mechanism is generally accepted. The diffusion coefficients were found to obey Eq. (1) with activation energies in the range of 2–2.6 eV. The prefactors D_0 were found to be very small, however, yielding D values of the order 10^{-10}–10^{-16} cm^2/s in the temperature range between 1100 and 700 K. More recent measurements were extended to 520 K. Diffusion constants of the order of 10^{-22} cm^2/s were deduced and the data were claimed to be consistent with phason-related mechanisms for diffusion at the lower end of the covered temperature regime [16].

It has recently been demonstrated that the NMR-monitored decay of the transverse nuclear spin magnetization [17,18] and 2D exchange NMR [19] provide a unique possibility to monitor the slow diffusion of resonant nuclei moving in a spatially inhomogeneous electric field gradient (EFG) in solids with disordered structures. Motional frequencies can be determined in cases when the motions are slow on the NMR signal frequency scale, typically in the sub-kHz range. As a direct consequence of the lack of translational periodicity in quasilattices, the spatial inhomogeneity of the EFG is an intrinsic property of QC's. The electric quadrupole interaction between the nuclei of spin $I > 1/2$ and the local EFG results in a strong inhomogeneous broadening of the NMR spectra in QC's, manifesting a continuous spatial variation of resonance frequencies, i.e., the resonant nuclei at different lattice sites have different resonance frequencies. The hopping of a nucleus from one lattice site to another thus provokes a change of its local environment and consequently a change of the resonance frequency. The same effect occurs if the environment of the resonant nucleus is changed via the motion of surrounding atoms.

In a 2D exchange NMR experiment the nuclear resonance frequency is monitored coherently two times—at the beginning and at the end of the "mixing" period t_{mix} [19,20]. The static nuclei with unchanged resonance frequencies during t_{mix} contribute to the diagonal intensity ($|\nu_1| = |\nu_2|$) of the 2D spectrum $I(\nu_1, \nu_2)$. The nuclei, which during t_{mix} jump to other lattice sites, however, create an off-diagonal intensity ($|\nu_1| \neq |\nu_2|$) in the inhomogeneously broadened 2D spectrum. The off-diagonal intensity is weak for a choice of t_{mix} much shorter than the characteristic time for atomic jumps τ_{exch} and thus the contours of the 2D spectral intensity appear as a narrow diagonal map whose length is determined by the inhomogeneous broadening. For long mixing times $t_{\mathrm{mix}} \gg \tau_{\mathrm{exch}}$ the off-diagonal intensity reaches saturation and the shape of contours depends on the actual type of atomic motion. For the restricted-space motion the contours adopt a diagonal shape and their width depends on the actually covered distance of the resonant nuclei in the confined space. This diagonal shape is characteristic of incommensurate structures [21] where the NMR frequency varies continuously in space as $\nu = \nu_0 + \sum_i \nu_i \sin(\vec{q}_i \vec{r} + \psi_i)$, the sum extending over all modulation waves. The same diagonal shape applies also to quasicrystals, following the arguments of Bak [22] who described the icosahedral structure as a multi-q structure with wave vectors $\vec{q}_i (i = 1, \ldots, 15)$ along the edges of an icosahedron. For bulk diffusion the contours are square shaped, demonstrating that the nuclei may reach any lattice site within the mixing-time interval [21]. The analysis of the off-diagonal intensity as a function of the mixing time thus allows one to extract the average time constant τ_{exch} for atomic jumps. Since the method cannot distinguish whether the shift of the resonance frequency is due to the motion of the probed nuclei or to configurational changes of their environment, $\tau_{\mathrm{exch}}^{-1}$ is an average jump rate for all the constituent atoms.

Our ^{27}Al 2D exchange NMR experiment was performed with the same $Al_{70}Re_{8.6}Pd_{21.4}$ sample that had been used in a previous ^{27}Al 1D NMR line shape and spin-lattice relaxation study [23] and which has been well characterized by measurements of thermal and transport properties [24,25]. The ^{27}Al NMR absorption line exhibits a strong inhomogeneous broadening of electric quadrupolar origin and the total spectrum extends over 3000 G at a frequency of 16.667 MHz. A three-pulse stimulated-echo 2D exchange pulse sequence was used. In spite of the extreme width of the total spectrum, the width of the central peak is only 30 KHz and a selective excitation at the center of the spectrum in a bandwidth of 200 KHz is sufficient for our purposes. Pure absorption 2D exchange spectra were recorded and the width $\Delta\nu_{\mathrm{exch}}$ of the inhomogeneously broadened line normalized to the contour length was extracted from the 2D contour plots. In Figs. 1a and 1b we show the plots for two mixing times t_{mix}, differing by 2 orders of magnitude. The frequency shift $\Delta\nu_{\mathrm{exch}}$ due to site exchange was determined for several choices of the mixing time and the average atomic jump time τ_{exch} was extracted from a fit using [20]

$$2\pi\Delta\nu_{\mathrm{exch}} = \sqrt{(1/T_2)^2 + [A \tanh(t_{\mathrm{mix}}/\tau_{\mathrm{exch}})]^2} \quad (2)$$

with A being a fit parameter. This formula takes into account that the width of the no-exchange ($t_{\mathrm{mix}} = 0$) spectrum is determined by the inverse spin-spin relaxation rate $(1/T_2)^{-1}$. For simplicity the probabilities for a given atomic jump and the reverse jump were assumed to be the same (symmetric exchange) giving a $\tanh(t_{\mathrm{mix}}/\tau_{\mathrm{exch}})$ dependence of the "dynamic" part of the linewidth [20]. Typically, six or seven experiments with different t_{mix} values were performed at each temperature and τ_{exch} was extracted from the fit with Eq. (2) as shown in Fig. 2. The experiments proved to be very time-consuming as a 2D experiment for a single t_{mix} value lasted from one to three days.

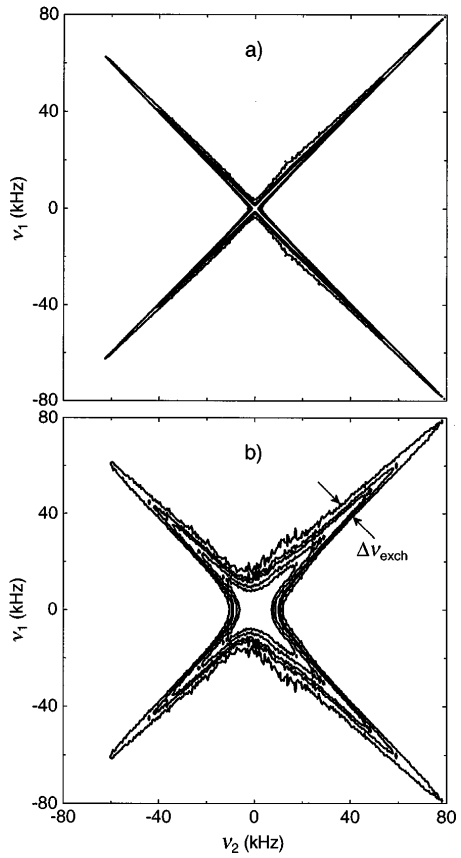

FIG. 1. Selectively excited ^{27}Al 2D exchange NMR spectra [$\nu_0(^{27}\mathrm{Al}) = 58.8$ MHz] of a $Al_{70}Re_{8.6}Pd_{21.4}$ icosahedral quasicrystal at $T = 5$ K for two different mixing times [(a) $t_{mix} = 10$ ms, (b) $t_{mix} = 1.5$ s]. The spectra are in the pure absorption mode and the contours appear as mirrored at the $\nu_1 = 0$ line due to the real Fourier transformation in the t_1 mode [19] of processing the time-domain data.

A particularly intriguing feature of the observed atomic motion in the Al-Re-Pd sample is the saturation of the width of the 2D exchange spectrum for mixing times satisfying the condition $t_{mix}/\tau_{exch} \gg 1$. The diagonal shape of the contours (see Fig. 1) of the saturated spectrum with a considerably larger width than the no-exchange spectrum demonstrates that the motion that we monitor is limited in space, extending over several interatomic distances only.

The temperature dependence of τ_{exch} was measured in the interval between 0.16 and 130 K. Below 4 K, the measurements were performed in a dilution refrigerator while above 4 K a continuous-flow ^{4}He cryostat was used. We may interpret τ_{exch}^{-1} as an average jump rate and relate it to a diffusion constant for this particular motion, given by $\mathcal{D} = l^2/\tau_{exch}$. Here l is the elementary jump length, which is of the order but smaller than the nearest neighbour distance in the QC structure, varying only insignificantly with temperature. We thus present τ_{exch}^{-1} versus T^{-1} on a double logarithmic plot in Fig. 3. The solid line is to indicate the overall temperature

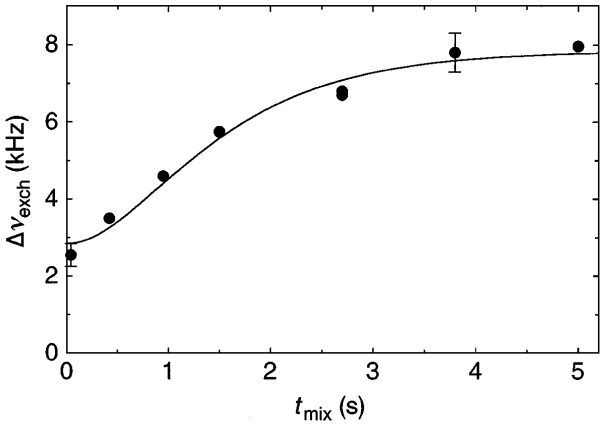

FIG. 2. The width $\Delta\nu_{exch}$ of the ^{27}Al 2D exchange NMR spectrum of $Al_{70}Re_{8.6}Pd_{21.4}$ as a function of t_{mix} at $T = 0.16$ K. The width has been measured at the position indicated by arrows in Fig. 1b on contours of equal length. The solid line represents the fit using Eq. (2), yielding $\tau_{exch} = 1.90$ s.

variation of τ_{exch}^{-1} or $\mathcal{D}$, respectively. Below 1 K, τ_{exch} is only weakly temperature dependent. At the lowest measured temperature of 0.16 K its value amounts to 1.9 s and it decreases only slightly to 1.67 s at 0.9 K. The temperature variation of τ_{exch} increases considerably between 0.9 and 30 K where τ_{exch} shortens by a factor of 50 from seconds into the tens of milliseconds range. Above 30 K the shortening of τ_{exch} shows again a tendency to saturation. The strong overall T dependence of τ_{exch} rules out the possibility that spin diffusion, a temperature-independent process, produces the dynamic broadening of the 2D exchange NMR spectra at least below 30 K. Our data may thus be taken as evidence for anomalous atomic motions, presumably initiated by phason flips as discussed above.

For estimating the magnitude of the diffusion coefficient $\mathcal{D}$ we take $l \approx 0.1$ nm as a typical distance for phason flips. Considering our values for $\tau_{exch}(T)$ we

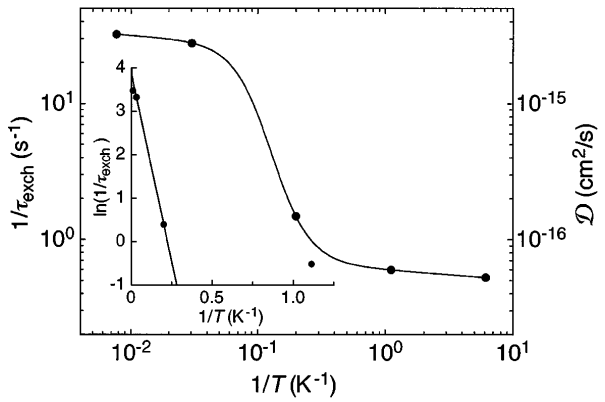

FIG. 3. τ_{exch}^{-1} versus T^{-1} on logarithmic scales. The solid line is to guide the eye. The inset, showing $\ln(\tau_{exch}^{-1})$ versus T^{-1}, allows one to estimate ϵ in Eq. (1) (see text).

obtain $\mathcal{D} \approx 5 \times 10^{-17}$ cm^2/s at 0.16 K and $\mathcal{D} \approx 3 \times 10^{-15}$ cm^2/s at 130 K. These values are many orders of magnitude larger than estimates for the bulk diffusion constant D based on extrapolating the data of high-T vacancy diffusion [13–15] for similar QC compounds or even the more recently claimed onset of phason-assisted bulk diffusion [16]. Although our data are scarce, we may estimate the characteristic energies related with the observed motions, assuming that they are thermally activated. This is done in the inset in Fig. 3 where $\ln(\tau_{\mathrm{exch}}^{-1})$ is plotted versus T^{-1}. The solid line is compatible with an activation energy $\epsilon = 1.5$ meV between 5 and 30 K. This energy should be compared with the assumption in Ref. [11] that the activation energy characterizing phason dynamics is of the order of $2k_B\theta_D$, where θ_D is the Debye temperature. For icosahedral Al-Re-Pd, $\theta_D = 378$ K [24] which leads to $\epsilon = 70$ meV, considerably larger than our estimated upper bound. Below 1 K, $\tau_{\mathrm{exch}}^{-1}$ tends to saturate, indicating a remanent motion of all the involved atoms, presumably due to quantum tunneling.

In summary, our ^{27}Al 2D exchange NMR experiments on an icosahedral $Al_{70}Re_{8.6}Pd_{21.4}$ QC have detected and identified slow atomic motions in the sub-kHz range at low and very low temperatures. The observed motion may be associated with phason flips confined to a spatially limited range. It can thus not directly be related to theoretical work predicting bulk atomic diffusion due to phason flips. We suggest that this motion should be regarded as a precursor to bulk diffusion, involving phason flips via quantum tunneling below 1 K and by thermal activation above. The behavior above 30 K needs further clarification.

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