

Atomic jumps in quasiperiodic  $\text{Al}_{72.6}\text{Ni}_{10.5}\text{Co}_{16.9}$  and related crystalline materialJ. Dolinšek,<sup>1</sup> T. Apih,<sup>1</sup> P. Jeglič,<sup>1</sup> M. Feuerbacher,<sup>2</sup> M. Calvo-Dahlborg,<sup>3</sup> U. Dahlborg,<sup>3</sup> and J. M. Dubois<sup>3</sup><sup>1</sup>*J. Stefan Institute, University of Ljubljana, Jamova 39, SI-1000 Ljubljana, Slovenia*<sup>2</sup>*Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany*<sup>3</sup>*LSG2M (UMR 7584), Centre d'Ingénierie des Matériaux, Ecole des Mines, Parc de Saurupt, F-54042 Nancy Cedex, France*

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<sup>27</sup>Al NMR measurements of the transverse magnetization decay in a decagonal quasicrystal  $\text{Al}_{72.6}\text{Ni}_{10.5}\text{Co}_{16.9}$  detected at temperatures between 300 and 4 K show slow, low-activation-energy, diffusive atomic jumps that exhibit properties compatible with the elementary excitations of the quasiperiodic lattices in the form of phason jumps. However, identical atomic motion was observed also in “vacancy-ordered” bcc crystalline  $\text{Al}_{50}\text{Cu}_{35}\text{Ni}_{15}$ , indicating that this motion is not quasicrystal specific, but a feature of close-packed atomic structures—either periodic or quasiperiodic—that contain structural vacancies.

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Low-energy excitations of quasicrystalline structures are predicted to exist in the form of “dynamical” phasons or phason flips, where an atom undergoes a diffusive jump to an energetically similar position on a small spatial scale of a fraction of an interatomic distance, creating there a matching-rules violation defect. In such a thermally excited local rearrangement of atoms no empty lattice sites are required, so that the process can take place in principle also in perfect, vacancy-free quasiperiodic lattices. The energy cost of creating these defects is due to misarrangement of atoms in the second coordination shell or beyond and hence cannot be high. As the activation energy for the atomic jump cannot be high either, phason flips are expected to be the dominant atomic motional degree of freedom in quasicrystals (QC's) at low temperatures, where conventional atomic transport mechanisms like vacancy-mediated diffusion are effectively frozen.

In order to identify phason flips experimentally, atomic motions in QC's were investigated with several techniques. Radiotracer diffusion measurements at temperatures above 700 K in icosahedral *i*-AlPdMn (Refs. 1–3) and *i*-AlCuFe (Ref. 4) as well as in decagonal *d*-AlNiCo (Refs. 5 and 6) have shown that at high temperatures the quasicrystalline diffusion is not significantly different from that in related crystalline metallic materials, for which a vacancy-mediated diffusion is generally accepted. The diffusion coefficients for various migrating atomic species (excluding aluminum) were found to be thermally activated with activation energies in the range 0.9–2.6 eV.<sup>3,4</sup> The diffusion of aluminum towards the surface of an *i*-AlCuFe crystal was measured during *in situ* oxidation experiments in the Auger scanning spectrometer<sup>7</sup> and the activation energy of 0.6 eV was estimated at temperatures below 750 K. Atomic motions at high temperatures (typically above 800 K), where atomic jumps take place on a picosecond time scale, were investigated by time-of-flight quasielastic neutron scattering experiments in *i*-AlCuFe (Refs. 8 and 9) and *i*-AlPdMn (Ref. 10) as well as in *d*-AlNiCo (Ref. 11). The appearance of a small Lorentzian foot at the elastic peak, developing gradually above 800 K, was attributed to the correlated simultaneous phason flips, which take place on a small spatial scale of a few tenths of a nanometer. However, a recent neutron experiment on a

“vacancy-ordered” bcc crystalline ( $\tau$ -phase)  $\text{Al}_{50}\text{Cu}_{35}\text{Ni}_{15}$  alloy<sup>12</sup> (in the following referred to as *t*-AlCuNi<sub>15</sub>) has detected similar picosecond atomic-jump dynamics at high temperature, suggesting that the observed atomic motion is not QC specific. Moreover, the activation energies for atomic jumps determined from the neutron data for *d*-AlNiCo [ $E_a \approx 0.55$  eV (Ref. 11)] and crystalline *t*-AlCuNi<sub>15</sub> [ $E_a = 0.60$  eV (Ref. 12)] are very similar and remarkably close to both the activation energy of atomic migration (0.61 eV) and the activation enthalpy for single-vacancy formation (0.67 eV) in pure aluminum.<sup>13</sup> It was also shown<sup>14</sup> that the structure of an ideal *d*-AlNiCo crystal exhibits a large amount of vacant atomic sites within closely spaced, half-occupied atomic columns (called columnar vacancies), which mediate atomic jumps and act as “pipes” for atomic diffusion within the 2-nm decagonal clusters. Columnar vacancies are not vacancies in the usual sense, as they arise from pairs of atomic columns that are too close in space to be fully occupied simultaneously. However, concerning atomic diffusion, they act in the same way as the usual vacancies. A very similar situation of columnar vacancies due to too closely spaced column pairs was observed also in the perovskite system SrTiO<sub>3</sub> (Ref. 15) either on the Ti or Sr sublattice, so that this property cannot be considered as QC specific, but rather as being specific to certain types of close-packed atomic structure, either periodic or quasiperiodic. The above considerations show that, based on the high-temperature experiments, the existence of QC-specific atomic jumps (phason flips), which would not exist also in periodic crystalline materials, is not that unambiguous as sometimes claimed.

The key problem in identifying phason jumps in QC's from the high-temperature experiments is the fact that at high temperatures this kind of motion interferes with other thermally excited, non-QC-specific atomic transfer processes, like the usual vacancy diffusion or the diffusion through channels in structures like the “half-vacancy pipes.” Since phason jumps are characterized by low activation energies, one could solve this problem elegantly by searching for phason jumps at low temperatures, where, on a given experimental time scale, the phason jumps are still excited, whereas all high-activation-energy conventional atomic

transport mechanisms should already be effectively frozen. The key to detect experimentally true phason jumps thus lies in the low-temperature experiments, such as below room temperature, by comparing quasicrystalline and related crystalline materials. A unique possibility to perform such experiments is provided by the NMR diffusion measurements in a spatially inhomogeneous electric field gradient (EFG) that is capable of detecting slow atomic motions on the subnanometric spatial scale. Slow, incoherent, low-activation-energy atomic jumps were indeed observed with this technique at low temperatures (from 400 to 4 K) in *i*-AlPdMn (Ref. 16) and at very low temperatures (down to 100 mK) in *i*-AlPdRe (Ref. 17). In this paper we report, by employing a Carr-Purcell echo-train experiment,<sup>18</sup> the detection of diffusive, low-activation-energy atomic jumps in decagonal Al<sub>72.6</sub>Ni<sub>10.5</sub>Co<sub>16.9</sub> (in the following referred to as *d*-AlNiCo<sub>16.9</sub>) at temperatures between 300 and 4 K. We show that although this motion exhibits properties compatible with phason jumps, it is not QC specific, as it exists also in vacancy-ordered bcc crystalline *t*-AlCuNi<sub>15</sub>.

The sensitivity of NMR to the incoherent random-walk atomic motions originates from the fact that the nuclear resonance frequency in a spatially inhomogeneous magnetic field or EFG changes with space: i.e., any atomic shift in space in the direction of the frequency gradient is accompanied by a change of the nuclear resonance frequency. In QC's the spatial inhomogeneity of the EFG is an intrinsic property of the quasiperiodic lattice. It arises from the nonperiodic distribution of the ionic and electronic charges and from the chemical disorder on the lattice. Consequently, the NMR spectra exhibit strong inhomogeneous broadening of electric-quadrupole origin. The sample originates from the same growths that were used in recent <sup>57</sup>Co radiotracer measurements.<sup>5</sup> Slow atomic diffusion in a spatially inhomogeneous EFG is conveniently investigated by measuring the NMR decay of the transverse nuclear spin magnetization.<sup>19</sup> In the case where the resonance frequency changes in space linearly (i.e., the frequency gradient  $\nabla\omega$  is constant), one obtains the spin-echo attenuation factor  $A(2\tau)$  in a two-pulse Hahn-echo experiment with a pulse separation  $\tau$  as<sup>19</sup>

$$A(2\tau) = \exp\left\{-\frac{2\tau}{T_2}\right\} \exp\left\{-D(\nabla\omega)^2 \frac{2\tau^3}{3}\right\}. \quad (1)$$

Here  $T_2$  is the spin-spin relaxation time describing the decay of the transverse magnetization in the absence of diffusion and  $D$  is the diffusion constant. The presence of diffusive motions results in a typical exponential-cubic  $\tau^3$  spin-echo amplitude decay. It is straightforward to check whether the  $\tau^3$  decay indeed originates from the incoherent, random-walk atomic motions by recording a Carr-Purcell (CP) echo train, where a sequence of  $2\tau$ -spaced echoes is created on the time axis  $t$ . The CP echo envelope decays with an exponent linear-in-time  $t$  (Ref. 18):

$$A(t) = \exp\left\{-\frac{t}{T_2}\right\} \exp\left\{-D(\nabla\omega)^2 \frac{2\tau^2 t}{3}\right\}, \quad (2)$$

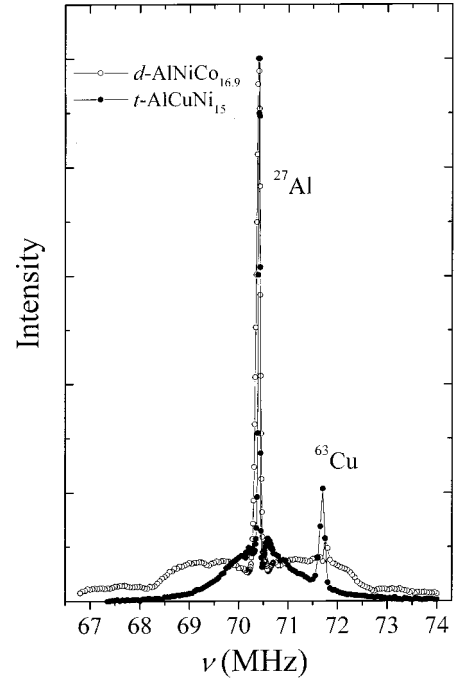


FIG. 1. <sup>27</sup>Al frequency-swept NMR spectrum of single-grain decagonal *d*-AlNiCo<sub>16.9</sub> (open circles, 10-axis  $\perp B_0$ ,  $T=4$  K) and polygrain crystalline *t*-AlCuNi<sub>15</sub> (solid circles,  $T=5$  K) in a field  $B_0=6.34$  T. The <sup>63</sup>Cu signal originates from the probe coil.

where the diffusion-induced attenuation [proportional to the effective damping constant  $D(\nabla\omega)^2\tau^2$ ] can be arbitrarily reduced or increased by changing the radio-frequency pulse separation parameter  $\tau$ , owing to the fact that the diffusive loss of magnetization takes place independently during each  $\tau$  interval.

It is interesting to consider whether the simple constant-frequency-gradient formulas of Eqs. (1) and (2) can be used to detect phason jumps in QC's, as there exists no long-range linear frequency variation in space on the quasiperiodic lattice. However, phason jumps are in principle small-scale atomic shifts for distances of a fraction of an interatomic distance. On such a scale, any frequency change in space due to the spatial inhomogeneity of the intrinsic EFG can be expanded in Taylor series, with the dominant linear term (i.e., a constant frequency gradient). In the presence of multiply connected jumps of the same atom, the constant-frequency-gradient formulas shall give valid description of the transverse magnetization decay for small diffusion times  $\tau$ , where the displacements of the resonant nuclei from their initial positions are still small, presumably less than one interatomic distance. Even in such a case, the constant frequency gradient  $\nabla\omega$  is not known yet for QC structures.  $\nabla\omega$  shall basically show a distribution of directions and magnitudes for different local atomic environments. Therefore only the product  $D_\omega = D(\nabla\omega)^2$ , which we shall name in the following as the "renormalized" diffusion constant (in units of  $\text{sec}^{-3}$ ), can be determined from the NMR transverse magnetization decay experiment. Moreover, as neither the distribution of  $\nabla\omega$  nor the anisotropy (the tensorial character) of  $D$  is known, we shall attempt to simplify the problem by analyz-

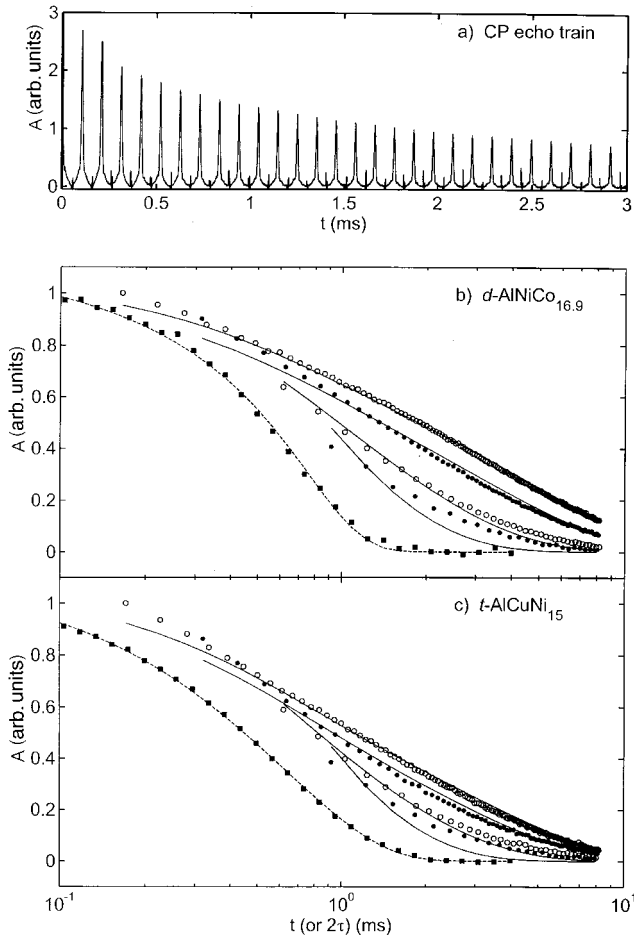


FIG. 2. Representative  $^{27}\text{Al}$  CP echo train of  $d\text{-AlNiCo}_{16.9}$  for  $\tau=50\ \mu\text{sec}$ . (b)  $^{27}\text{Al}$  CP echo-train envelopes for different  $\tau$ 's (solid and open circles, from top to bottom:  $\tau=25, 50, 100, 150\ \mu\text{sec}$ ) and Hahn-echo decay data (squares) of  $d\text{-AlNiCo}_{16.9}$  at  $T=100\ \text{K}$ . Solid and dashed lines are fits described in the text. (c) Identical experiment performed on crystalline  $t\text{-AlCuNi}_{15}$  ( $T=100\ \text{K}$ ). The horizontal axis denotes time  $t$  for the CP data and  $2\tau$  for the Hahn-echo data.

ing the CP echo-train data with a single average  $D_\omega$  renormalized diffusion parameter with the aim of proving its true diffusional character by varying its attenuation strength on the transverse magnetization decay through the variation of the pulse-spacing parameter  $\tau$ .

The CP and Hahn-echo decay experiments were performed on the  $d\text{-AlNiCo}_{16.9}$  sample at temperatures from 300 to 4 K. A  $\pi/2$  pulse of  $2\ \mu\text{sec}$  length was used. In order to vary systematically the diffusion attenuation of the echoes, the  $^{27}\text{Al}$  CP echo trains [Fig. 2(a)] were recorded for four interpulse spacing times  $\tau=25, 50, 100,$  and  $150\ \mu\text{sec}$ . Typical echo-envelope  $A(t)$  data at  $T=100\ \text{K}$  are collected in Fig. 2(b), where it is observed that the CP trains with larger  $\tau$ 's decay increasingly faster, whereas the Hahn echo shows the fastest decay of all. There exists a large difference between the CP curve with the shortest  $\tau=25\ \mu\text{sec}$  (which exhibits the smallest diffusion damping) and the Hahn-echo curve, where the diffusion damping is the strongest, thus supporting the diffusive nature of the detected atomic mo-

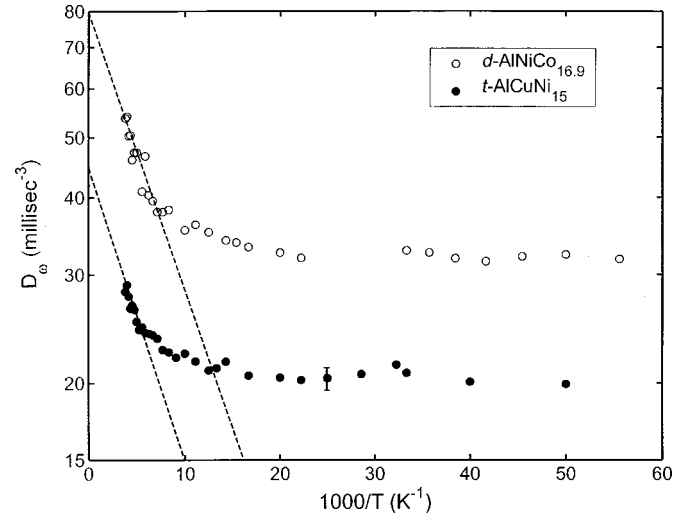


FIG. 3. Temperature dependence of the renormalized diffusion constant  $D_\omega$  of  $d\text{-AlNiCo}_{16.9}$  (open circles) and crystalline  $t\text{-AlCuNi}_{15}$  (solid circles). Only the data above 16 K are shown (the data between 16 and 4 K are a continuation of the temperature-independent plateaus below 50 K). The activation energies were estimated from the high-temperature data (dashed lines).

tions. The data were analyzed by first reproducing the shape of the CP decay curve with the shortest  $\tau=25\ \mu\text{sec}$ , assuming that it corresponds to a good approximation to the pure  $T_2$  decay with no diffusion attenuation. The best fit was obtained by a sum  $a_{T_2}(t) = a_1 \exp(-t/T_2^{(1)}) + a_2 \exp(-t/T_2^{(2)})$ . Using this form of the  $T_2$  decay, the diffusion damping was then determined at each temperature by fitting the complete set of four CP curves simultaneously using the ansatz  $A(t) = a_{T_2}(t) \exp\{-D_\omega 2\tau^2 t/3\}$ , where, due to different  $\tau$ 's, each CP curve has its own effective diffusion damping parameter  $D_\omega \tau^2$ . The theoretical fits [solid lines in Fig. 2(b)] reproduce the experimental points reasonably well by using a single value of the renormalized diffusion constant  $D_\omega$ , as well as the same  $T_2$ -decay parameters. The applicability of the constant-gradient formulas in the fit procedure demonstrates that, on the diffusion time scale of our CP experiment ( $0 \leq \tau \leq 150\ \mu\text{sec}$ ), the detected motion takes place on a small spatial scale, presumably less than one interatomic distance. The  $T_2$ -decay parameters  $T_2^{(1)}=5.3\ \text{msec}$ ,  $T_2^{(2)}=0.61\ \text{msec}$ ,  $a_1=68\%$ , and  $a_2=32\%$  were found to be temperature independent within the experimental precision, whereas the temperature-dependent renormalized diffusion constant  $D_\omega$  is displayed in Fig. 3. Below about 70 K there is no noticeable variation of  $D_\omega$  with temperature, whereas above 70 K,  $D_\omega$  starts to increase gradually. A small activation energy of  $E_a=9\ \text{meV}$  was determined from the high-temperature data between 120 and 300 K (dashed line in Fig. 3). The detected atomic motion is thus a low-activation-energy process. Here we assumed that the temperature dependence of  $D_\omega = D(\nabla\omega)^2$  originates primarily from the “true” diffusion constant  $D$ , whereas the temperature variation of the frequency gradient  $\nabla\omega$  due to lattice thermal expansion (where, upon heating, the interatomic distances increase, making  $\nabla\omega$  smaller and hence provoking just opposite temperature de-

pendence of  $D_\omega$  as that displayed in Fig. 3) is a minor effect. In the Hahn-echo experiment the diffusion time scale is much larger than in the CP experiment; in our case, it extends over the interval  $0 \leq \tau \leq 4$  msec. The fit of the Hahn-echo data with Eq. (1) [dashed line in Fig. 2(b)] yields a factor of 6 smaller  $D_\omega$  parameter, demonstrating the gradual breakdown of the constant-gradient approximation on a longer diffusion time scale.

Summarizing the above results, the NMR-detected atomic motion in  $d$ -AlNiCo<sub>16.9</sub> at temperatures between 300 and 4 K is slow, of low-activation-energy, of diffusive character, and survives to low temperatures. These features are compatible with the properties of phason jumps. However, in order to represent true elementary low-energy excitations of QC structures, the motion should be QC specific and should not exist also in related periodic crystalline materials. In order to check for this possibility, we conducted identical NMR experiment on crystalline  $t$ -AlCuNi<sub>15</sub>, whose structure consists of a rhombohedrally deformed cubic Al lattice with the Cu/Ni atoms and vacancies in the cube centers:<sup>12</sup> i.e., it is a vacancy-ordered bcc crystal. This material contains up to few at. % of vacant lattice sites due to stability reasons—the vacancy concentration regulates the density of valence electrons that stabilize the structure electrostatically.<sup>20</sup> The <sup>27</sup>Al NMR spectrum of the  $t$ -AlCuNi<sub>15</sub> crystal (Fig. 1) exhibits about a factor of 2 smaller inhomogeneous broadening than

the  $d$ -AlNiCo<sub>16.9</sub> crystal, suggesting that the frequency gradients in both compounds are of similar order of magnitude. The CP and Hahn-echo experiments [Fig. 2(c)] in the  $t$ -AlCuNi<sub>15</sub> crystal show identical features as in the  $d$ -AlNiCo<sub>16.9</sub> crystal—the presence of diffusion damping of spin echoes due to slow, low-activation-energy, diffusive atomic motion. The fits [solid lines in Fig. 2(c)] were again made with temperature-independent  $T_2$ -decay parameters ( $T_2^{(1)} = 3.5$  msec,  $T_2^{(2)} = 0.53$  msec,  $a_1 = 58\%$ , and  $a_2 = 42\%$ ), whereas the temperature-dependent  $D_\omega$  is shown in Fig. 3. Here  $D_\omega$  exhibits a similar activation energy of  $E_a \approx 9$  meV in the high-temperature regime above 150 K as  $d$ -AlNiCo<sub>16.9</sub>.

The above results demonstrate that though the NMR-detected atomic motions in  $d$ -AlNiCo are compatible with phason jumps, they are *not* OC specific, but are identically found also in the related crystalline  $t$ -AlCuNi that contains structural vacancies of the same type as QC's—vacancies contribute to the electrostatic stabilization of the structure. The observed atomic motion thus appears to be a feature of close-packed atomic structures—either periodic or quasiperiodic—that contain structural vacancies.

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