

## Tunneling State Anisotropy in a Single Grain Decagonal Quasicrystal

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We present low-temperature measurements, between 20 mK and 20 K, of the sound velocity variations in a single grain of the decagonal quasicrystal Al-Ni-Co. We have used acoustic shear waves of frequency 70 MHz propagating in the quasicrystalline planes with two different polarizations: parallel and perpendicular to the quasicrystalline planes. Our results show the presence of tunneling states (TSs) with a strong difference of the phonon-TS coupling for the two polarizations, which reveals a strong anisotropy of distribution of the orientations of the TSs in the sample. This result gives direct evidence that TSs are generated by the quasicrystalline structure itself.

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The low-temperature properties of amorphous materials reveal an excess of low energy excitations in comparison to crystals. In the tunneling state model [1,2], these excitations arise from the tunneling of some groups of atoms between slightly degenerate configurations. Such configurations could indeed exist in amorphous matter because of the disorder of the structure, as shown in structural glass simulations [3]. However, the microscopic nature of those tunneling states (TSs) is still an open question. In this respect, the investigation of quasicrystals, materials which are long-range ordered without any translational symmetry, is an interesting issue to clarify the role played by periodicity, or its missing, for the existence of TSs. Several recent experiments showed the presence of tunneling states in icosahedral quasicrystals of the highest structural quality, Al-Pd-Mn [4,5], Al-Cu-Fe [6], and Zn-Mg-Y [7], with a density of states similar to that of metallic glasses. Moreover, the acoustic study of a poor quality Al-Li-Cu icosahedral phase revealed that the TS density of states increases when the structural quality of the sample is improved by annealing [8]. From these results, one is inclined to conclude that TSs are intrinsic to quasicrystals just like they are intrinsic to glassy structures. In this Letter, we report on low-temperature velocity measurements of acoustic waves with defined polarizations which bear evidence of a strong TS anisotropy in a single grain decagonal quasicrystal. This result evidences the fact that TSs are intrinsic to quasicrystalline structures and, besides, gives some salient features of TSs at the microscopic level.

Decagonal quasicrystals combine periodicity, along one direction which is a tenfold symmetry axis, and quasiperiodicity in the planes perpendicular to the periodic direction. Therefore, they provide a unique opportunity to extract the effect of quasiperiodicity alone by comparing, in the same sample, the physical properties in the quasicrystalline planes and along the periodic axis. Strong anisotropies have actually been found for the electrical re-

sistivity [9,10], thermal conductivity [11,12], optical [13], and mechanical [14] properties, revealing the specificity of the quasicrystalline state. The low energy excitations in decagonal quasicrystals were, however, seldom investigated. In Ref. [12], the authors report on measurements of the low-temperature thermal conductivity in a single grain Al-Cu-Co decagonal phase, both in the quasicrystalline planes and along the periodic axis. After subtracting an estimate of the electronic contribution, they found a nearly  $T^2$  dependence for the lattice thermal conductivity in a small temperature range below about 1 K. This behavior could arise from the scattering of phonons by tunneling states. However, the analysis of these measurements is difficult because of the large electronic contribution at low temperature and the existence of TSs in decagonal quasicrystals remains questionable. Besides, since thermal conductivity measurements involve all phonon polarizations for one direction of propagation, such measurements are not well designed to reveal any possible TS anisotropy. Here, we present low-temperature sound velocity measurements for acoustic waves with defined polarizations which allow us to probe directly the TSs.

The quasicrystal  $\text{Al}_{72}\text{Ni}_{13.5}\text{Co}_{14.5}$  used for this paper was grown at IFF in Jülich. The starting Al-Ni-Co alloy was produced by levitation melting in a water-cooled Cu crucible under Ar atmosphere. It was then remelted under vacuum and solidified by the Bridgman technique. The resulting ingot contained several centimeter-sized grains which were clearly seen on a polished cross section in a polarized light microscope. One of these grains was mechanically extracted and oriented with the Laue x-ray diffraction method. It had finally the shape of a  $9 \times 9 \times 5 \text{ mm}^3$  slab with two opposite faces perpendicular to the tenfold symmetry axis. For the sample composition a partial superstructure ordering in the periodic direction is typical and is manifested by the layers of diffuse scattering corresponding to the double (i.e., about 0.8 nm) periodicity [15].

The elastic properties are expected to be isotropic in the quasiperiodic plane because of its symmetry strictly higher than four. The transverse elastic isotropy was checked experimentally and the remaining five independent elastic moduli,  $c_{11}$ ,  $c_{33}$ ,  $c_{13}$ ,  $c_{44}$ , and  $c_{66}$ , were measured in an Al-Ni-Co decagonal quasicrystal [16]. Experimentally, we used transverse waves which give pure shear strains in order to enhance the effect of a possible anisotropy. This choice leaves two independent relevant velocities,  $v_{\parallel} = \sqrt{c_{66}/\rho}$  and  $v_{\perp} = \sqrt{c_{44}/\rho}$ , where  $\rho$  is the density of the sample.  $v_{\parallel}$  is obtained for both the direction of propagation and the polarization in the quasiperiodic planes, and  $v_{\perp}$  is obtained for the propagation in the quasiperiodic plane and the polarization along the tenfold axis. For the emission and reception of the acoustic waves, two piezoelectric AC-cut quartz transducers were glued with silicone grease on two opposite faces perpendicular to the quasiperiodic planes. When excited on their fundamental resonant frequency the transducers generate pure 70 MHz shear waves. A manufacturer's mark on the transducers indicates the direction of polarization. With this setup the acoustic waves propagate in the quasicrystalline planes and, to get the two different polarizations, we just had to rotate the piezoelectric quartz by  $90^\circ$ , at room temperature, without unsticking them. The sound velocity variations were measured as a function of temperature with a phase-sensitive method. The sample was cooled in a  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator.

Figure 1 shows the sound velocity variations measured as a function of temperature between 20 mK and 4.2 K. For both polarizations, the sound velocity increases with the logarithm of the temperature until about 1 K, where it reaches a maximum. Above 6 K the sound velocity decreases approximately linearly with temperature, as shown in Fig. 2.

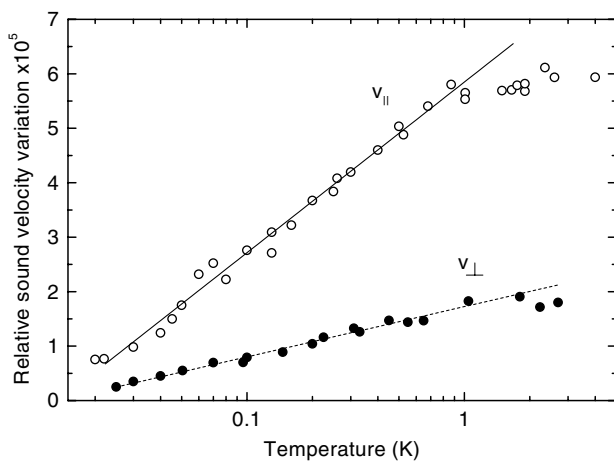


FIG. 1. Semilogarithmic plot of the low-temperature sound velocity variations in  $d$ -AlNiCo for 70 MHz shear waves propagating in the quasiperiodic plane with a polarization perpendicular ( $\bullet$ ) and parallel ( $\circ$ ) to the quasiperiodic plane. The curves are shifted arbitrarily. The solid and dashed lines are logarithmic fits of the data below 1 K.

At low temperatures, the logarithmic increase of the sound velocity, which extends over two decades in temperature, is strong evidence of the existence of TSs in the sample. In the tunneling state model, it arises from the resonant interaction of the TSs with the incident acoustic wave. This resonant process leads to the variation of the sound velocity [17]

$$\Delta v/v = C \ln(T/T_0), \quad (1)$$

where  $T_0$  is an arbitrary reference temperature and the tunneling strength  $C$  is related to the TS density of states  $P$  and the mean TS-phonon coupling  $\gamma$  by  $C = P\gamma^2/\rho v^2$ . The electrical resistivity along the periodic direction of decagonal quasicrystals is metalliclike and, in the quasicrystalline planes, it is quantitatively similar to that of metallic glasses [10]. Thus, there are free electrons to relax the TSs. This channel of relaxation is efficient even at the lowest temperatures and results in an additional contribution  $\Delta v/v = -C/2 \ln(T/T_0)$ , i.e., the measured logarithmic slope is actually equal to  $+C/2$  as in metallic glasses. The logarithmic fits of the data below 1 K (solid and dashed lines in Fig. 1) lead to  $C_{\parallel} = 2.7 \times 10^{-5}$  and  $C_{\perp} = 0.8 \times 10^{-5}$ . At 4.2 K, we measured the absolute velocities  $v_{\parallel} = 4.68 \times 10^3 \text{ m} \cdot \text{s}^{-1}$  and  $v_{\perp} = 4.19 \times 10^3 \text{ m} \cdot \text{s}^{-1}$ , in perfect agreement with the velocities deduced from the density  $\rho = 4186 \text{ kg} \cdot \text{m}^{-3}$  and the elastic moduli  $c_{66}$  and  $c_{44}$  measured at 5 K in Ref. [16]. We can thus calculate the coupling parameters for both polarizations,  $P\gamma_{\parallel}^2 = 2.5 \times 10^6 \text{ J} \cdot \text{m}^{-3}$  and  $P\gamma_{\perp}^2 = 0.6 \times 10^6 \text{ J} \cdot \text{m}^{-3}$ .

The coupling parameter for the polarization in the quasiperiodic plane is similar to those found in high quality icosahedral quasicrystals or in metallic glasses for shear waves. For instance,  $P\gamma^2 = 2.1 \times 10^6 \text{ J} \cdot \text{m}^{-3}$  in an Al-Cu-Fe icosahedral phase [6] and  $P\gamma^2 = 3.2 \times 10^6 \text{ J} \cdot \text{m}^{-3}$  [18] in an Al-Pd-Mn icosahedral phase [4]. Unfortunately it is not possible to measure separately  $P$  and  $\gamma$  in

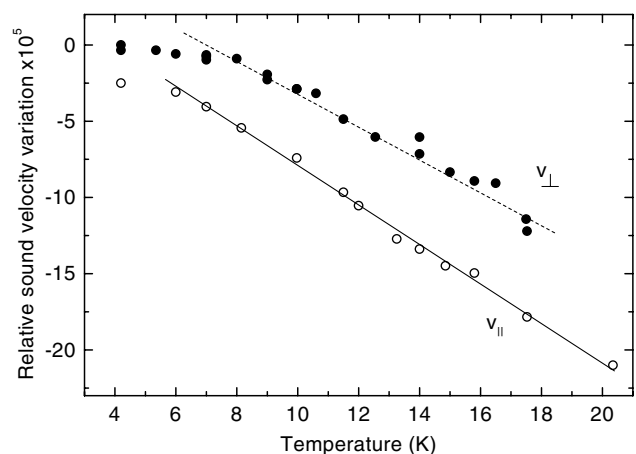


FIG. 2. Linear plot of the high-temperature sound velocity variations in  $d$ -AlNiCo with the same notations as in the caption of Fig. 1. The solid and dashed lines are the best linear fits of the data above the maximum.

normal conducting metallic alloys. However, the coupling constant  $\gamma$  is a local deformation potential and it is not expected to vary much among solids with the same type of binding. Hence, from similar coupling parameters, we deduce that the particular order of the “forbidden” symmetry, decagonal or icosahedral, has probably little effect on the TS density of states. The existence of TSs seems to be a universal property of quasicrystals and all high quality quasicrystals seem to have similar TS densities of states.

The coupling parameter  $P\gamma_{\perp}^2$  for waves polarized along the periodic axis is much smaller. We get the large anisotropy factor  $P\gamma_{\parallel}^2/P\gamma_{\perp}^2 = 4.2$ , where obviously  $P$  does not depend on the polarization. To analyze the meaning of this anisotropy, we have to go back to the microscopic definition of the coupling constant  $\gamma$ . In the tunneling state model, some groups of atoms experience a potential which is a double well in the configuration space. The tunneling state results then from the coupling of the two corresponding configurations by tunneling effect. The main effect of an elastic strain is to modify the asymmetry  $\Delta$  of the double-well potential [19], i.e., the coupling constant for one TS is defined as

$$2\gamma_{ij} = \partial\Delta/\partial e_{ij}, \quad (2)$$

where  $e_{ij}$  is the strain field. For a given direction of propagation  $i$  and polarization  $j$  of the incident phonons in the reference frame of the decagonal quasicrystal, the measured tunneling strength for one particular TS is

$$C_{ij} = P\gamma_{ij}^2/(\rho v_{ij}^2). \quad (3)$$

The coupling tensor, defined here in the reference frame of the sample, can be conveniently described by its three eigenvalues,  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$ , and the three Euler angles which define the corresponding three perpendicular eigenvectors. This description defines the orientation of the TS which can therefore be considered as an elastic dipole [20]. In the simple case of the tunneling motion of one single atom between two positions, the axis of the dipole is simply the direction of the motion. Hence, in Eq. (3),  $\gamma_{ij}^2$  is a function of the three eigenvalues and the three Euler angles. One needs now to average this quantity over all the TS orientations. In glasses the orientations of the TSs are random and hence the averaging leads to a macroscopic coupling constant  $\gamma_i^2$  for transverse waves which does not depend on the directions of polarization or propagation of the acoustic waves [21]. On the contrary, our finding that the coupling constant depends on the direction of the polarization of the shear waves proves that the distribution of the TS orientations is anisotropic in decagonal quasicrystals. If we take into account only the elastic isotropy of the quasicrystalline planes and make the reasonable assumption that the two eigenvectors perpendicular to the dipole axis have equal eigenvalues, we find

$$\gamma_{\parallel}^2/\gamma_{\perp}^2 = \tan^2\theta/4, \quad (4)$$

where  $\theta$  is the angle formed by the periodic direction and the TS direction. From  $\gamma_{\parallel}^2/\gamma_{\perp}^2 = 4.2$ , we deduce  $\theta = 76^\circ$ . Therefore, the TSs in our decagonal sample almost lie in the quasicrystalline planes. This result emphasizes the specificity of quasicrystallinity. It is the specific quasicrystalline atomic arrangement which generates the tunneling states.

There exists very few mentions in the literature of such an anisotropic coupling constant. Yet, there is a good coherence with a former acoustic study of sodium ions in  $\beta$ -alumina single crystal [22]. This material has a hexagonal symmetry and consists of a stacking along the  $c$  axis of layers of spinel-like blocks of alumina. The space between these layers can accommodate a large excess of  $\text{Na}^+$  ions which are responsible for a two-dimensional ionic conductivity. Thermal conductivity and heat capacity experiments in this disordered crystal showed the existence of TSs which are likely to arise from the tunneling of the  $\text{Na}^+$  ions within the conducting planes [23,24]. With an acoustic method similar to ours, the authors of Ref. [22] later measured  $\gamma_{\parallel} = 0.17$  eV much larger than  $\gamma_{\perp} = 0.05$  eV for shear waves polarized in the plane of easy diffusion and along the  $c$  axis, respectively.

At higher temperatures, the approximately linear decrease of the sound velocity observed in this study (see Fig. 2) is also a common feature of glasses, disordered crystals, and icosahedral quasicrystals (for a review, see Ref. [25]). This behavior is most likely related to the plateau in the thermal conductivity and the peak in the heat capacity observed in glasses in the same range of temperatures. A detailed analysis of these higher energy excitations would require one to study the frequency dependence of the sound velocity [26] and to extend the measurements to higher temperatures. Yet, we can draw some conclusions from our measurements. From the linear fits of the data (solid and dashed lines in Fig. 2) we deduce the slopes  $\beta_{\parallel} = -1.5 \times 10^{-5} \text{ K}^{-1}$  and  $\beta_{\perp} = -1.1 \times 10^{-5} \text{ K}^{-1}$  for the two polarizations of the acoustic waves. These slopes are similar to  $\beta = -1.7 \times 10^{-5} \text{ K}^{-1}$  measured in an Al-Pd-Mn icosahedral quasicrystal [4] but 1 order of magnitude smaller than those for an Al-Cu-Fe icosahedral phase [6] or for metallic glasses [25]. There have been several theoretical attempts to give a unified description of the low- and high-temperature phenomena in glasses. For instance, the same entities could be responsible for both behaviors if one introduces a crossover at a few degrees Kelvin from coherent tunneling to thermally activated process [27] (in addition to soft harmonic excitations in the soft potential model [28]) or to incoherent tunneling [29]. Our measurements show that the slopes in Fig. 2 are much weakly dependent on the orientation of the polarization,  $\beta_{\parallel}/\beta_{\perp} = 1.4$ , than those in Fig. 1, where  $C_{\parallel}/C_{\perp} = 3.4$ . Thus, this result contradicts, at least for quasicrystals, a direct proportionality between the tunneling strength and the linear slope as it was proposed phenomenologically [25] or as it is expected for a crossover of the same defects from tunneling to thermal activation

[27]. Indeed, in this latter case, the coupling of the defects with the acoustic wave should have the same angular dependence, whether the defects are in the tunneling or the thermal activation regime.

It is tempting to relate the TSs of quasicrystals to another dynamics specific to quasicrystals, the so-called phason jumps. Within Penrose-like tiling models, phason jumps can be viewed as local configuration flips. Evidence of such a phason dynamics has been found in neutron scattering experiments in the Al-Cu-Fe and Al-Pd-Mn icosahedral quasicrystals and, recently, also in the Al-Ni-Co decagonal quasicrystal (see [30] and references therein). So far, these specific atomic hoppings were found to be active only for high temperatures, i.e., for instance, above 500 °C for decagonal Al-Ni-Co. However, one should note that, in the interpretation of Coddens *et al.*, this energy scale is related to a thermally activated assisting process that enables the phason jumps. The phason jumps themselves involve much lower energy barriers. Their relaxation times are indeed found to be very short ( $\sim 10^{-12}$  s) and independent of temperature, in the temperature range where they are observed. On the other hand, the hopping distances reported so far, between 0.2 and 0.4 nm, are far too large to allow the tunneling. Thus it is, at present, unclear if there is, at all, a connection between the low and high energy localized excitations in quasicrystals. It would, however, be a major issue in understanding the specific dynamics of quasicrystals.

In conclusion, we have studied the sound velocity variations at low temperature in a single grain decagonal quasicrystal. Our results show the presence of TSs as in the case of high quality icosahedral quasicrystals. Besides, by studying two differently polarized acoustic waves, we found a strong anisotropy of the TS phonons coupling constant which reveals that the TSs belong to the quasicrystalline planes. Together with the conclusion of Ref. [8] that the TS density of states increases with the perfection of the quasicrystalline order, this leaves very few doubts that TSs are intrinsically generated by quasicrystalline atomic arrangements. This anisotropy, which is reported here for the first time in nonperiodic solids, is well explained by considering the dipolar nature of the TSs. These are well described as 1/2 spins, but not as free spins. They are rather spins on a local anisotropy axis. The distribution of the orientations of these axes is random in a glass but anisotropic in decagonal quasicrystals.

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