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Tunneling states in a single-grain Al-Cu-Fe quasicrystal

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Velocity and attenuation of acoustic waves (190 Mhz) have been measured in a phason-free single grain of *i*-AlCuFe between 40 mK and 30 K. The results reveal the existence of tunneling states (TS's). The coupling parameter $P\gamma^2$ (where P is the TS density of states and γ is the phonon-TS coupling) is close to the one in metallic glasses. The crossover temperature from the T^3 law to the plateau regime in the attenuation is well defined. Hence, within the TS model, both P and γ can be calculated. The TS's seem to be intrinsic to the quasicrystal structure.

At low temperatures amorphous materials are known to exhibit very distinct physical properties as compared to crystals. These properties are usually explained within the tunneling-state model proposed by Anderson *et al.*[1] and Phillips.[2] However this model is purely phenomenological and gives no information on the microscopic nature of these tunneling states (TS's). To understand the nature of the disorder responsible for the particular properties of amorphous materials it is tempting to study materials with intermediate order. Quasicrystals are good candidates for this purpose: they are long-range ordered, unlike disordered materials, but contrary to crystals this order is not translational.

Few measurements of the acoustic properties of quasicrystals at low temperatures have been performed and no general answer could be found as for the presence of tunneling states in these materials. This strongly contrasts with the universality of the results in amorphous materials. Former studies of three stable icosahedral quasicrystals AlCuFe, AlLiCu, and AlPdMn by various authors revealed very different behaviors. The velocity variation of $Al_{65}Cu_{20}Fe_{15}$ at low temperature did not show the usual TS signature, but the sample was not a single-grain quasicrystal.[3] In AlLiCu a small density of states of TS's was found,[3,4] and in the best quasicrystalline sample studied, AlPdMn, TS's were found with a density of states close to the one in amorphous metals.[5] However, in the latter experiment there was a magnetic field effect on the behavior of the acoustic properties, and this raises questions about the intrinsic nature of the observed TS's.

To examine the question of the existence of intrinsic TS's in perfect quasicrystals we report here on acoustic measurements in a single-grain, single phase of a perfect icosahedral quasicrystal AlCuFe. Our results show unambiguously the presence of elastic TS's with a coupling constant similar to those found in amorphous metals and in *i*-AlPdMn. Besides, the TS density of states P and the phonon-TS coupling γ have been measured separately. Both values are similar to those found in amorphous metals. To our knowledge this is the first determination of both these quantities separately in quasicrystalline materials.

The single-grain quasicrystal was obtained by starting from a master alloy of nominal composition $Al_{63}Cu_{25}Fe_{12}$ prepared by levitation melting in a helium atmosphere. Starting metals were of purity 99.99 wt. % Al, 99.99 wt. % Cu, and 99.95 wt. % Fe. The alloy has been rapidly quenched by planar flow casting, resulting in brittle flakes about 20 mm thick and 5–10 mm wide. Flakes were annealed in an alumina crucible under vacuum for 4 days at 860 °C just below the peritectic transformation, and rapidly cooled. This process leads to the growth, in the partially melted alloy, of grains of the icosahedral phase that can reach several millimeters and present a pentagonal dodecahedral morphology. These grains can be extracted from the solidified ingot which also contains regions with crystalline phases.

The single grain used in this study was characterized by a complete neutron diffraction study.[6] The high structural perfection of the sample was ascertained by studying the profiles of the diffraction peaks. The full widths at half maximum are independent of the perpendicular momentum and correspond to the instrumental resolution. The profiles are only due to the instrumental divergence. The mosaicity of the single grain is $\sim 0.05°$, which corresponds to a single crystal of very good quality for a metallic alloy. No additional reflection or diffuse scattering could be detected. These results imply a perfect quasicrystal without any phason strain. This sample may be compared to the best Al-Pd-Mn icosahedral single grains, which are not often obtained.

The sample was shaped to obtain two parallel faces, which were separated by 1.35 mm. Y-cut quartz transducers were glued to these faces. They generated pure acoustic shear waves at 190 MHz when excited on their third harmonic. The signal consisted of acoustic pulses of 150 ns duration with a repetition rate varying between 0.1 and 30 Hz depending on temperature, to avoid any heating of the sample. The variation of the sound velocity was measured with a phase-sensitive device. The sample was cooled down to 40 mK in a He^3-He^4 dilution refrigerator. A magnetic field of up to 5 T was produced by a superconducting magnet.

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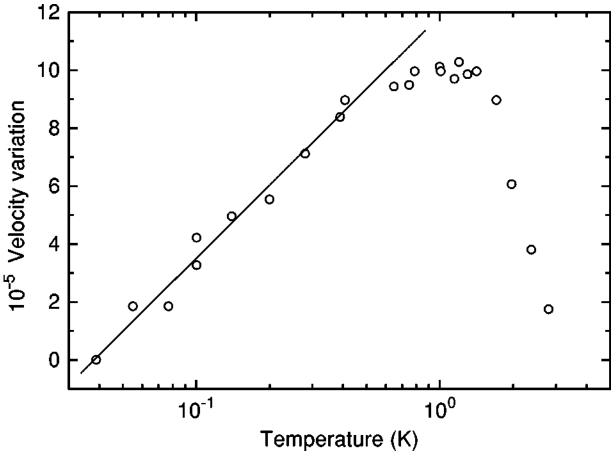

FIG. 1. Velocity variation as a function of temperature, for 190 MHz shear acoustic waves in a single grain of *i*-AlCuFe quasicrystal. The velocity reference is the velocity at the lowest temperature $T_0 = 39$ mK. The solid line is the best fit to Eq. (1).

Figure 1 shows the sound velocity variation as a function of temperature below 4 K. The velocity increases with the logarithm of the temperature from 40 mK to 1 K where it reaches its maximum. Above 4 K it decreases linearly up to at least 30 K as shown in Fig. 2. These variations are typical of disordered matter (for a review see Ref. 7). The logarithmic variation is the signature of the TS's. They have been introduced to explain the low-temperature properties of disordered matter.[1,2] A resonant interaction between them and the acoustic wave gives a variation of the acoustic velocity V according to[8]

$$\frac{V_i(T)-V_i(T_0)}{V_i(T_0)} = \frac{P\gamma_i^2}{\rho V_i^2}\ln\left(\frac{T}{T_0}\right), \tag{1}$$

where P is the density of states of the TS's, γ is a deformation potential which describes the coupling of the acoustic wave with the TS's, ρ is the specific mass, T_0 is a reference temperature, and the subscript i holds for t transverse or l longitudinal waves. In our sample we have $\rho = 4400\ \mathrm{kg\,m^{-3}}$ and $V_t = 3.6\times 10^3\ \mathrm{m\ s^{-1}}$. From Eq. (1) and the logarithmic slope of Fig. 1 we deduce a coupling parameter $P\gamma_t^2 = 2.1\times 10^7\ \mathrm{erg\,cm^{-3}}$. This value is very similar to the one found in *i*-AlPdMn (Ref. 5) ($P\gamma_t^2 = 1.6\times 10^7\ \mathrm{erg\,cm^{-3}}$) with the same experimental method. It is also close to the usual coupling constants in amorphous metals, a typical case of which is *a*-PdSi where $P\gamma_t^2 = 1.9\times 10^7\ \mathrm{erg\,cm^{-3}}$.[9]

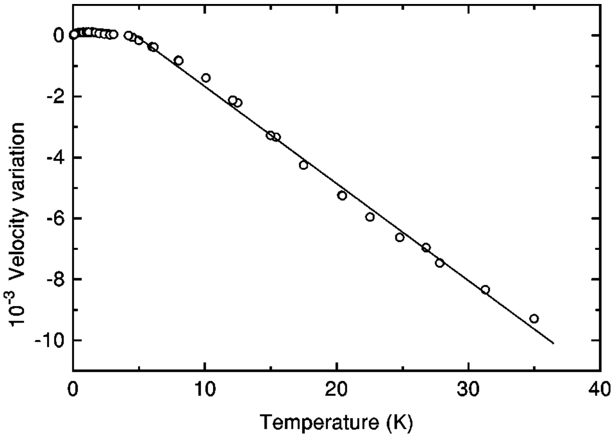

FIG. 2. Velocity variation as a function of temperature above 1 K, for 190 MHz shear acoustic waves in a single grain of *i*-AlCuFe quasicrystal. The velocity reference is the velocity at the lowest temperature $T_0 = 39$ mK. The solid line is the best linear fit.

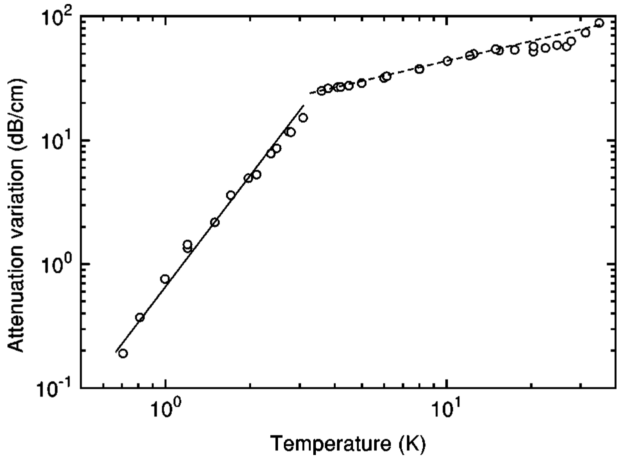

FIG. 3. Attenuation variation as a function of temperature, for 190 MHz shear acoustic waves in a single grain of *i*-AlCuFe quasicrystal. The curve is arbitrarily shifted to have a zero attenuation at T=0 K. The solid line is a T^3 law. The dashed line is a linear law [see Eq. (3)].

At higher temperatures the linear decrease of the acoustic velocity with increasing temperatures is also a common feature of amorphous materials[10] and also of quasicrystals.[3] By contrast a power law is observed in crystals in this temperature range. Thermally activated processes can give such a linear law.[10] However, it has been shown that these processes do not account well for the observed frequency dependence of the velocity variation.[10] This behavior has also been explained within the framework of the phenomenological model of the soft atomic potential, which predicts a crossover from TS's to excitations of higher energies around 5 K.[11] Discussion of the origin of this linear law is out of the scope of this report. Nevertheless, since this effect is characteristic of disordered matter, it is interesting to compare our results with other studies. Some results obtained in various materials show a linear temperature dependence of the sound velocity.[12] In amorphous solids the slopes are in a range extending from $\beta = -0.3\times 10^{-4}\ \mathrm{K^{-1}}$ to $\beta = -7.2\times 10^{-4}\ \mathrm{K^{-1}}$. The smallest slopes in absolute value correspond rather to amorphous metals and the highest rather to amorphous insulators. Thus, the slope we measured here $\beta = -3.2\times 10^{-4}\ \mathrm{K^{-1}}$ (Fig. 2) resembles more the one in amorphous insulators. This value is nearly one order of magnitude larger than the one obtained in a former study of a i-AlCuFe sample of different composition and in polygrain structure.[3]

The results for the acoustic attenuation are reported in Fig. 3. At low temperature the attenuation follows a T^3 law (the solid line in Fig. 3). At $T_m = 3.6$ K there is a sharp change towards a linear law (the dashed line in Fig. 3). Above 15 K the curve deviates from the linear variation, and this is due probably to some additional thermally activated processes.

The linear behavior of the attenuation can arise from thermally activated processes. Assuming that these processes have relaxation times following the Arrhenius law

$$\tau = \tau_0 \exp(E_a / k_B T), \tag{2}$$

and taking a distribution of activation energies E_a roughly flat, the relaxation attenuation is found to be[13]

$$\Gamma = C \omega T, \tag{3}$$

where C is a constant depending only on the material and proportional to the distribution of the energy barriers of the activated processes. Taking the slope of the linear variation shown in Fig. 3 and using Eq. (3), we calculate $C = 2.2 \times 10^{-9}$ dB cm^{-1} s K^{-1}, which is close, for instance, to the slope found in amorphous selenium.[14] However, the subtraction of this contribution from the attenuation leaves a constant attenuation above T_m. This plateau and the T^3 law are well explained within the TS model.[15] The processes giving these behaviors are TS relaxation assisted by phonons. The crossover temperature T_m from the power law to the plateau satisfies the condition[15]

$$\omega \tau_{min}(2 k_B T_m) \sim 1, \tag{4}$$

where $\tau_{min}(E)$ is the relaxation time of a TS of energy E (i.e., the splitting of its fundamental doublet) associated with a symmetrical double-well potential. For a one-phonon relaxation mechanism (which is the main one at low temperature) one gets[15]

$$\tau_{min}^{-1}(E) = \left(\sum_i \frac{\gamma_i^2}{V_i^5} \right) \frac{E^3}{2 \pi \rho \hbar^4} \coth\left(\frac{E}{2 k_B T} \right). \tag{5}$$

Our results exhibit a well-defined crossover temperature at $T_m = 3.6$ K. Using the value of $P\gamma_t^2$ obtained from the velocity variation at low temperatures and the fact that $V_l \gg V_t$ ($V_l = 7.2 \times 10^5$ cm s^{-1} according to Ref. 16), Eq. (4) yields $P = 2.1 \times 10^{32}$ erg^{-1} cm^{-3} and $\gamma_t = 0.2$ eV.

Unlike *i*-AlPdMn,[5] we observe no change in both the attenuation and velocity variations when a 5 T magnetic field is applied. Thus, there is no doubt as to the elastic nature of the TS's responsible for our results.

It is interesting to compare our values with those found in amorphous matter. In fused silica, with the same method, one obtains $P = 0.83 \times 10^{32}$ erg^{-1} cm^{-3} and $\gamma_t = 0.65$ eV.[17] The comparison with amorphous metals is more difficult because the TS's are strongly relaxed by the electrons, and the attenuation is not due to the phonon-TS coupling alone. Hence, we cannot use the same method to separate the two parameters P and γ. However, by choosing an amorphous superconductor the specific heat can be measured and gives a TS density of states of $n = 2.7 \times 10^{33}$ erg^{-1} cm^{-3}.[18] This parameter is not the same as our parameter P, because there is a large distribution of the TS relaxation times, and it is not the same TS's which are observed in a specific heat measurement or in an acoustic experiment. With typical values of the different parameters one finds $n = 10 \times P$, i.e., $P = 2.7 \times 10^{32}$ erg^{-1} cm^{-3}.[19] As a consequence, from the slope of the sound velocity one obtains $\gamma_t = 0.25$ eV. Hence, the TS parameters P and γ we obtain in *i*-AlCuFe are very close to those obtained in amorphous metals. However, there are at higher temperatures several differences with amorphous metals which must be underlined. At first, the slope β of the linear temperature dependence of the acoustic velocity (Fig. 2) is higher than in amorphous metals. Then, the acoustic attenuation in amorphous metals shows a linear temperature dependence at low temperature corresponding to the relaxation of the TS's by electrons. By contrast, in *i*-AlCuFe a T^3 law is observed and explained by the relaxation of the TS's by phonons like in amorphous insulators. This can be correlated with the very high resistivity of high-quality quasicrystals[20] and could be explained by a strong localization of the electrons which are therefore unable to relax the TS's.

We can get a new insight into the TS's in quasicrystals from our results. Unlike AlPdMn where the magnetic field acts on the TS's,[5] AlCuFe does not exhibit such an effect. The behavior of AlPdMn in a magnetic field can be explained not by a change of the TS density of states with the magnetic field but rather by a change of the TS coupling due to some magnetoelastic coupling with magnetic impurities. Apart from this magnetic effect, both these two high-quality quasicrystals show nearly the same acoustic properties at low temperatures. In other respects, our results differ strongly from the ones obtained in a former study of *i*-$Al_{65}Cu_{20}Fe_{15}$ by a vibrating-reed technique where TS's are not observed.[3] However, it has often been noticed that the physical properties of quasicrystals are highly sensitive to the composition, preparation, and quality of the samples. In this respect, the sample of Ref. 3 was not of the same composition as ours and it was not a single grain, which means it was not free from defects. The comparison of our results with those in AlLiCu can be more significant because this material has been also studied in a single-grain form.[4] TS's have been observed in these materials and they have been correlated with the amplitude of phason strain, i.e., the quality of the samples: The coupling parameter increases with the amplitude of the phason strains but it always remains smaller by nearly one order of magnitude than the one we measured in *i*-AlCuFe.[4] Thus, the TS's observed in AlLiCu could be considered as arising from phason strain. Besides, it is known that even the best AlLiCu samples do not reach the structural quality (defined by the width of the diffraction peaks) of the high-quality AlCuFe or AlPdMn samples. Unlike AlLiCu, AlCuFe seems to have a TS density of states which increases with the quasicrystalline quality. There could exist in this quasicrystal free of phason strain intrinsic tunneling states, and the tunneling of these states could be quenched by the phason strain, i.e., by the defects introduced in the quasicrystalline structure.

To conclude, we have observed tunneling states in a single grain of AlCuFe quasicrystal. The grain was a perfect quasicrystal without any phason strain. The density of states and the TS-phonon coupling have been measured and are close to the ones in amorphous metals. The comparison of our results with former studies shows that, contrary to quasicrystals with internal phason strain, there are intrinsic tunneling states in quasicrystals free of phason strain.

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