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Tunneling systems and disorder in quasicrystals

Norman O. Birge, B. Golding, W. H. Haemmerle, H. S. Chen, and J. M. Parsey, Jr.
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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Atomic tunneling has been found in icosahedral ribbons of Al_5Li_3Cu and $Mg_3Zn_3Al_2$, as well as in a single-grain equilibrium quasicrystal of $Al_{5.1}Li_3Cu$, from measurements of the low-frequency sound velocity and damping below 1 K. The density of states of tunneling systems depends on the sample preparation and correlates with the amplitude of phason strain in the samples. The extent of disorder in quasicrystals is appreciably closer to that of crystals than to metallic glasses.

Since the discovery of rapidly quenched Al-Mn alloys with long-range icosahedral order by Shectman, Blech, Gratias, and Cahn[1] there has been a large effort by many workers[2] to understand the structure and physical properties of this new class of materials. One area of intense study is the defect structure of the quasicrystals. The observations that x-ray diffraction peaks are broad[3] and shifted from their theoretical positions[4] showed that the materials are substantially disordered—they are not perfect quasicrystals in the original sense of Levine and Steinhardt.[5] In addition to affecting structural measurements, this disorder should also play a role in determining the physical properties of quasicrystals. One knows that in highly disordered systems such as glasses the disorder changes the nature of the elementary excitations; the low-temperature properties of such systems are dominated by the presence of atomic tunneling systems,[6] which should not exist in perfect crystals. To investigate the role and the extent of the disorder in quasicrystals, we have measured the low-temperature sound velocity and damping of several different quasicrystalline materials, including a large (≈ 0.5 cm) single grain of icosahedral (i-) $Al_{5.1}Li_3Cu$.[7] We have also measured several related crystalline phases, which have been proposed to be comprised of the same building blocks as the icosahedral phases.[8]

In this paper we report our measurements from 0.005 to 10 K on the compounds $Mg_3Zn_3Al_2$ and Al_5Li_3Cu in both their quasicrystalline and crystalline Frank-Kasper[9] phases. Our results are summarized as follows: (1) We have observed unambiguously the presence of atomic tunneling systems (TS) in an Al_5Li_3Cu quasicrystal ribbon, in a large, single-grain $Al_{5.1}Li_3Cu$ equilibrium quasicrystal, and also in a superconducting $Mg_3Zn_3Al_2$ quasicrystal ribbon. (2) The low-energy density of states of TS depends on the sample preparation conditions—it is higher in rapidly quenched ribbons than in the slowly cooled equilibrium sample. (3) The magnitude of the phason strain in the samples also depends on the preparation, and correlates with the density of states of TS. (4) Quasicrystals have surprisingly little disorder; the densities of states of TS are closer to those of related crystals than to those of metallic glasses. We do not include here our measurements of the quasicrystals i-$Al_{74}Si_6Mn_{20}$ or i-$Pd_{58.8}U_{20.6}Si_{20.6}$,[10] because the low-temperature properties may be influenced by the magnetic behavior of these systems.[11,12]

The icosahedral ribbons of i-Al_5Li_3Cu and i-$Mg_3Zn_3Al_2$ prepared by melt spinning, have a thickness of 15–20 μm and a width of 1–2 mm. The grain sizes in the samples range from 1 to 10 μm, therefore we are measuring the elastic properties averaged over the orientations of many grains. The single-grain quasicrystal of $Al_{5.1}Li_3Cu$ was grown by vertical gradient freezing, with an interface velocity of only 2 mm/h. Crystalline ribbons of cubic $Mg_3Zn_3Al_2$ and α-$Al_{72.5}Si_{10.1}Mn_{17.4}$ were prepared by annealing originally quasicrystalline ribbons. Bulk crystalline samples of cubic $Mg_3Zn_3Al_2$ and cubic Al_5Li_3Cu, the latter a single crystal, were grown slowly from the melt. For the bulk materials, experimental reeds were cut with a string saw or spark cutter, then polished to a thickness of 50–125 μm. The Young's modulus sound velocity v_E and the damping were measured with a vibrating-reed technique.[13] A typical reed in our experiment had a length of 0.4 cm and a fundamental resonance frequency of 0.3–2 kHz. Changes in the sound velocity were measured to better than a part in 10^6, and changes in the damping to a few percent.

Figure 1 shows the variation in the sound velocity versus temperature for Al_5Li_3Cu in three different forms: a quasicrystal ribbon, a single-grain quasicrystal, and a single crystal. In all three samples the sound velocity varies as $\log T$ at the lowest temperatures, reaches a maximum, and then decreases nearly linearly with temperature. This behavior is qualitatively similar to that found in metallic glasses, as seen in the data on the metallic glass $Pd_{78}Si_{16}Cu_6$ (Ref. 14) shown in Fig. 1 with a compressed vertical scale. In contrast, we expect defect-free crystals to have a temperature-independent sound velocity in this temperature region.

Figure 2 shows the variation in sound velocity versus temperature for three different samples of $Mg_3Zn_3Al_2$: a quasicrystal ribbon, an annealed crystalline ribbon, and a bulk crystalline sample. All of these samples are superconducting, with transition temperatures of 0.42, 0.39, and 0.32 K, respectively.[15] Again the sound velocity varies as $\log T$ at the lowest temperatures, reaches a maximum (near 0.05 K), and exhibits a kink near T_c. The sound velocity maximum shifts to slightly higher temperatures at higher overtone frequencies. Figure 2 also shows data for $Cu_{60}Zr_{40}$,[14] a superconducting metallic glass with $T_c \approx 0.4$ K, for comparison. The metallic-glass data are again plotted on a compressed scale to show their qualita-

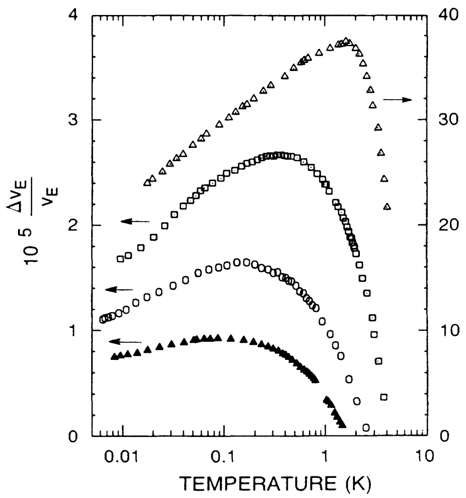

FIG. 1. Relative change in sound velocity vs log temperature for four normal metallic samples: the metallic glass $Pd_{78}Si_{16}Cu_6$ (Δ) at 1.0 kHz (Ref. 14), a quasicrystalline ribbon of i-Al_5Li_3Cu (□) at 1.0 kHz, a single-grain quasicrystal of i-$Al_{5.1}Li_3Cu$ (○) at 2.7 kHz, and a single crystal of cubic Al_5Li_3Cu (▲) at 2.3 kHz. The vertical scale of the metallic glass data has been compressed by a factor of 10. The vertical zero is arbitrary.

tive similarity to the quasicrystal data.

The changes in sound velocity evident in Figs. 1 and 2 are due to the interaction of atomic tunneling systems with phonons and electrons, as described by the tunneling model.[6] There are two types of interaction between phonons and tunneling systems, resonant and relaxational.

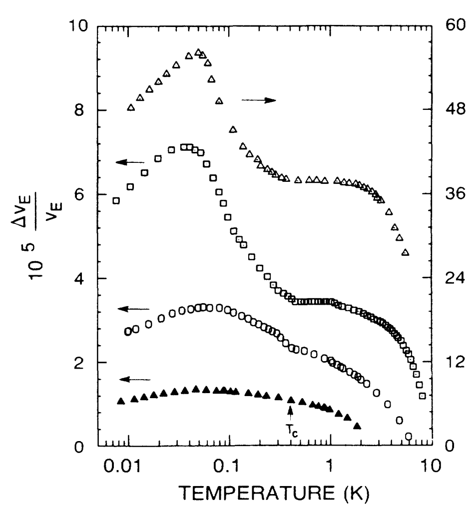

FIG. 2. Relative change in sound velocity vs log temperature for four superconducting samples ($T_c \approx 0.4$ K): the metallic glass $Cu_{60}Zr_{40}$ (Δ) at 1.6 kHz (Ref. 14), a quasicrystalline ribbon of i-$Mg_3Zn_3Al_2$ (□) at 0.3 kHz, an annealed crystalline ribbon of cubic $Mg_3Zn_3Al_2$ (○) at 0.6 kHz, and a bulk crystalline sample of cubic $Mg_3Zn_3Al_2$ (▲) at 0.7 kHz. The vertical scale of the metallic glass data has been compressed by a factor of 6.

At low temperatures, the resonant interaction causes the sound velocity to vary in temperature as $\Delta v/v = C\ln(T/T_0)$.[16] The constant C is equal to $P\gamma^2/\rho v^2$, where P is the density of TS per unit energy and volume, γ is a characteristic coupling constant or deformation potential between TS and phonons, ρ is the density of the material, and v is the velocity of sound. The velocity changes due to the relaxational interaction depend on the value of ωT_1, where ω is the measuring frequency and T_1 is the shortest relaxation time of the TS with energies near kT.[17] In a normal metal at low temperatures, the TS relaxation rates are dominated by interactions with conduction electrons.[18] Low-frequency measurements stay in the regime $\omega T_1 \ll 1$, and the relaxational contribution to the temperature dependence of the sound velocity is of the form: $\Delta v/v = -(C/2)\ln(T/T_0)$. Since the effects on the sound velocity of the two types of interaction are additive, the sound velocity of a normal metallic glass at low temperatures should have a positive logarithmic slope equal to $C/2$. Above ≈ 1 K, the sound velocity decreases rapidly as a result of phonon-mediated relaxation processes. These features are seen in Fig. 1.

In a superconductor the TS relaxation rate decreases rapidly just below T_c due to the gap, causing the sound velocity to increase as T is lowered.[19] The sound velocity reaches a maximum when the TS relaxation rate becomes comparable to the measurement frequency, i.e., $\omega T_1 \approx 1$. At the lowest temperatures only the effects of the resonant interaction is observed. These features are seen in Fig. 2.

At kilohertz frequencies the damping is dominated by relaxational processes, while the resonant contribution is negligible.[17] In both normal and superconducting metals there is a plateau where the damping has the value $(\pi/2)C$. Only at the very lowest temperature does the damping drop in the superconducting samples, when $\omega T_1 \gg 1$. The behavior of our damping data is in accord with this picture.

We can extract the value of C for our samples both from the logarithmic slope of the sound velocity at low temperatures, and from the value of the damping in the plateau region. We have not subtracted any residual from the damping data. Table I displays the results for crystals, quasicrystals, and metallic glasses. The data are ordered with the TS density of states increasing from top to bottom.

A significant feature of the data in Table I is the presence of TS in every sample; perfect crystalline behavior is the exception rather than the rule in condensed matter systems. According to the tunneling model,[6] the tunneling systems responsible for the behavior seen in Figs. 1 and 2 originate in the low-energy tail of a broad distribution of potential barriers. The observed density of states of TS at low energies can be affected by changes in either the width or the height of that distribution, due respectively to strain fields or to the density of defects.

One possible source of defects and strain fields is grain boundaries. However, the grain sizes in the ribbons range from 1 to 10 μm. If we assume that grain boundaries are a few atomic layers thick, then the volume fraction of grain boundary in these samples is only 0.01–0.1%. To explain the acoustic data as arising from excess defects at

TABLE I. Tunneling parameters from low-temperature acoustic properties.

Structure	Material	10^5C from velocity	10^5C from damping
Bulk crystals	Cubic $Mg_3Zn_3Al_2$	0.15	0.5
	Cubic Al_5Li_3Cu	0.20	0.5
Single grain quasicrystal	i-$Al_{5.1}Li_3Cu$	0.36	0.76
Annealed crystalline ribbons	Cubic $Mg_3Zn_3Al_2$	0.43	0.64
	α-$Al_{72.5}Si_{10.1}Mn_{17.4}$	0.4	1.0
Quasicrystal ribbons	i-$Mg_3Zn_3Al_2$	1.4	1.0
	i-Al_5Li_3Cu	0.7	1.2
Metallic glasses[a]	Glassy $Pd_{78}Si_{16}Cu_6$	6.5	8.7
	Glassy $Cu_{60}Zr_{40}$	5.8	9.7

[a]Reference 14.

grain boundaries, either the density of such defects, or their coupling constants, would have to be much larger than those found in the bulk of metallic glasses. Moreover, the presence of TS in the single-grain quasicrystal $Al_{5.1}Li_3Cu$ and the single-crystal Al_5Li_3Cu proves that grain boundaries are not the sole source of strain in these materials. There must be enough intrinsic strain in these samples to produce the distribution of potential barriers discussed above.

Various models have been proposed to account for defects in the quasicrystal structure, including dislocations[20] or quenched phason strains.[21] Recent results show a strong correlation between diffraction peak widths and phason momentum, indicating that most of the disorder is in the phason degrees of freedom.[22] A connection between phason strain and TS in quasicrystals is supported by two distinct trends in the data. First, the quasicrystal ribbons show higher densities of states of TS than the single-grain quasicrystal. The amplitude of phason strain in a sample can be determined by measuring the shift in the positions of certain x-ray peaks. We have analyzed the x-ray peak positions of our samples, and found that the quenched ribbons have about five times more phason strain than the single-grain quasicrystal.[23] Second, the single-grain quasicrystal i-$Al_{5.1}Li_3CU$ contains a higher density of states of TS than the single-crystal cubic Al_5Li_3Cu. Both of these samples were formed by cooling very slowly from the melt. The excess of TS in the quasicrystal compared to the crystal suggests that a mechanism for disorder exists in the quasicrystal which has no counterpart in the crystal. Phason strain is such a mechanism.

Thus far we have emphasized the disorder in the quasicrystals. But perhaps the most striking feature of Table I is the relatively small amount of disorder in the quasicrystals. *The density of states of TS in quasicrystals is significantly closer to that of crystals than to that of metallic glasses.* This observation puts constraints on any model of quasicrystal disorder, such as the "icosahedral glass,"[24] a random packing of icosahedra.

In conclusion, we have observed atomic tunneling systems in normal and superconducting quasicrystals, in ribbons, and in a large single-grain sample. The data indicate a correlation between internal phason strain and the density of states of tunneling systems. They also show that quasicrystals are surprisingly ordered; they resemble crystals more than metallic glasses with regard to tunneling centers. We believe that measurements of this type, when correlated with microstructural information, will lead us to a better understanding of the disorder in quasicrystals as well as in crystalline and glassy metals.

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