Phonon-Assisted Tunneling in Bismuth Tunnel Junction*

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We report the first observation of phonon-assisted tunneling in a semimetal-insulator tunnel junction, represented by remarkably fine structure in the conductance-voltage curve at low temperatures. This process gives rise not only to structure near zero bias, as in the case of the semiconductor tunnel diode, but also to several conductance peaks near the edge of a new band at voltages corresponding to the band edge plus the phonon energies. The existence of phonon-assisted tunneling, resulting from the conservation of the transverse momentum, thus provides a useful method for locating band-edge energies by tunneling spectroscopy. We establish, for the filled electron and hole bands of pure bismuth, four band edges: $+90\pm5$, $+38\pm2$, -35 ± 3, and -60 ± 5 meV; and less reliably, nine additional band edges: $+650$, $+145$, -80, -110, -140, -200, -600, -800, and -1600 meV, where $+$ and $-$ refer to below and above the Fermi level, respectively.

WE have observed fine structure in the conductance curves of monocrystalline Bi-Al-$_2O_3$-Au tunnel junctions. Analysis of the data clearly indicates that such structure arises from phonon-assisted tunneling. This process is particularly important near the edge of a new band, where it gives rise to a conductance peak at a voltage corresponding to the band edge plus the relevant phonon energy. Thus phonon-assisted tunneling plays a key role in determining band-edge energies in Bi by tunneling spectroscopy.[1]

The tunnel junctions were fabricated on a polished and then etched surface (trigonal or bisectrix) of pure-Bi single crystals by successive evaporation of sapphire (Al_2O_3) and gold, using an electron-beam gun. The vacuum system with a mask changer enabled us to make eight junctions of a small piece of single crystal in one operation without breaking vacuum. Each junction has an area of $5<10^{-4}$ cm^2. The tunneling resistance was controlled by adjusting the amount of oxide deposited on the junction area. All junctions whose resistance exceeded 5 kΩ displayed fine structure.

Figure 1 shows several conductance curves up to about ±200 mV. Units 311-11 and 308-2 are two typical monocrystalline Bi junctions. For comparison, the data from units *S*-65 and *E*-42 are also displayed in the same figure. Unit *S*-65, which had been reported previously,[1] showed only limited structure, whose general features are similar to those of the new units. Unit *E*-42 exhibited smeared structure at low voltages, which is typical of polycrystalline junctions (made by evaporating Bi onto an oxidized strip of Al). All the curves represent data taken at 1.4°K, except for the dashed line, which depicts measurements made at ~80°K. Throughout this report, positive bias will mean that the Au electrode is at a higher potential than the Bi. Figure 2 shows the conductance plot for Unit 311-11 on expanded voltage scales in the neighborhood of zero bias and over the range from 0 to 120 mV. It is apparent that each conductance curve contains a large number of identifiable bumps, of which the "tunneling spectrum" is composed. In Fig. 3, we display these bumps for seven units, including the old one, *S*-65. Hatched regions correspond to relatively broad peaks. The junction plane is bisectrix for Unit 317-4 and trigonal for all the other units.

In carefully examining the structure near zero bias of more than fifty units (mostly trigonal), we found that, if any bumps were detected at all, they appeared at only four distinct voltages: 3 ± 1, 6 ± 1, 10 ± 1, and 14 ± 1 mV, regardless of the polarity of the applied voltage. These four voltages, designated as A, B, C, and D respectively, in Fig. 2, correspond closely to the measured[2] phonon energies of the four modes in the trigonal direction: transverse acoustic (TA)=4.8, longitudinal acoustic (LA)=7.4, transverse optic

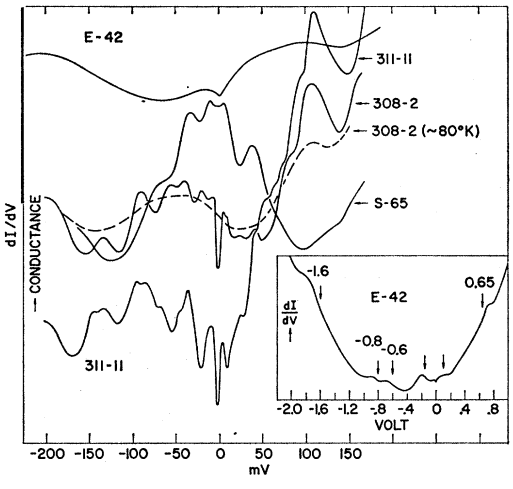

FIG. 1. Conductance curves ($+V$ corresponds to Bi negative) for two new monocrystalline Bi junctions 311-11 and 308-2, together with the previously published *S*-65 and a polycrystalline Bi junction *E*-42. The solid curves are data taken at 1.4°K. The conductance curve for *E*-42 at high voltages is shown in the insert. The ordinate scale is linear, and the units are arbitrary.

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[1] L. Esaki and P. J. Stiles, Phys. Rev. Letters 14, 902 (1965).

[2] J. L. Yarnell, J. L. Warren, R. G. Wenzel, and S. H. Koenig, IBM J. Res. Develop. 8, 234 (1964); D. B. Smith, J. L. Warren, and J. L. Yarnell, Bull. Am. Phys. Soc. 12, 689 (1967).

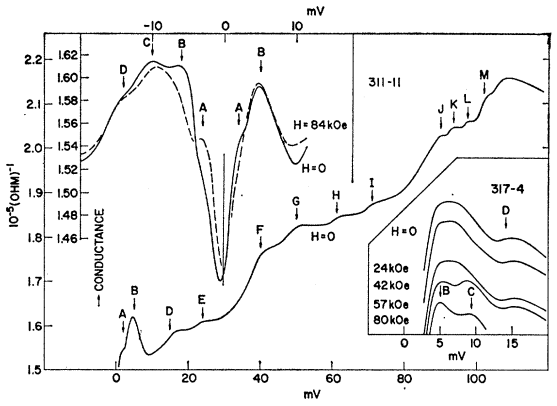

FIG. 2. Conductance curves on expanded voltage scales. The effect of an applied magnetic field up to 84 kOe is shown in two inserts (the upper left and lower right corners).

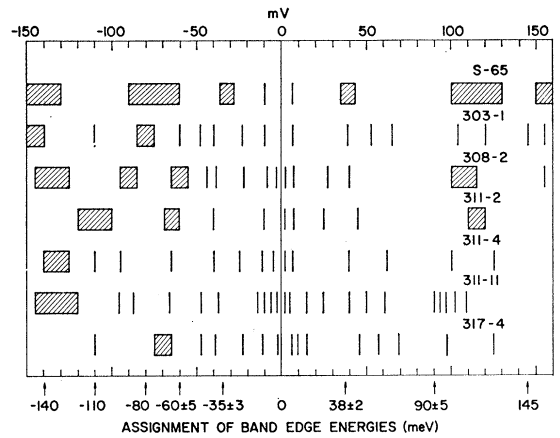

FIG. 3. Tunneling spectra for seven units and assignment of band-edge energies. Note that the band edges of the partially filled valence and conductance bands do not appear in the spectrum, as explained in the text.

(TO)=12.6, and longitudinal optic (LO)=13.4 MeV at the zone boundary and $TO=9.2$ and $LO=12.5$ MeV at the zone center. We believe that each of the observed bumps signifies the threshold of the phonon-assisted tunneling associated with one of the phonon modes.[3] When the applied voltage is high enough for the tunneling electron to emit a phonon, a new channel for tunneling opens up, with a resulting increase in the tunneling current and a peak in the conductance curve.

In addition to the marked phonon peaks near zero bias, we often saw relatively weak bumps at around ±25 mV, for instance, E in Fig. 2. These weaker bumps are probably due to multiphonon processes. Thus the present observations in the neighborhood of zero bias are reminiscent of phonon-assisted interband tunneling in semiconductors.[4] In Bi tunnel junctions, however, not only the partially filled conduction and valence bands but also other bands are expected to contribute to the tunneling current, and we have indeed found the phonon-assisted process to be equally significant for tunneling into these higher and lower bands. This is clearly seen in Fig. 2 near 40 and 90 mV. There is a band just below each of these two voltages. The bumps F and G for one band, and J, K, L, and M for the other band are due to phonon-assisted tunneling; the weaker bumps H and I probably arise from multiphonon processes, although one cannot dismiss the possibility that the tunneling electrons are exciting oxide-layer phonons.[5] It is very important to note that, choosing the higher band-edge energy to be 88 meV, the voltage differences from the band edge to J, K, L, and M are almost identical to the voltages of A, B, G, and D. Therefore we now have a method of determining band-edge energies with greater accuracy than before. We simply note the lines common to all spectra, as in Fig. 3, and subtract the phonon energies. We see four band edges: +90±5, +38±2, −35±3, and −60±5 MeV, which were previously estimated to be +105, +35, −30, and −60 MeV, respectively. The latter two bands are probably the ones recently observed by Antcliffe and Bate,[6] although their values are somewhat lower than ours. We can say further, but with less confidence, that there are also band edges at ∼+145 MeV (previously, +150 MeV) and at ∼−80, ∼−110, and ∼−140 MeV (previously, −135 MeV). It should be noted that one does not observe phonon bumps corresponding to the band edges of the partially filled electron and hole bands. The reason for this is that the threshold for phonon-assisted tunneling for a partially filled band is just the phonon energy, rather than the band edge plus the phonon energy.

The conductance dip at zero bias, usually not symmetric, became about 15% deeper as the temperature was lowered from 4.2 to 1.4°K. The magnitude of the dip in Unit 311-11 or 308-2 can be used to obtain a rough estimate of the ratio of phonon-assisted tunneling to direct tunneling in the neighborhood of zero bias. The considerable difference in relative intensity among units for a particular phonon process produces a variety of shapes for the conductance curve, as seen in Fig. 1. From Fig. 3, we note a tendency for the 3±1-MeV (A) and 6±1-MeV (B) phonons to be predominant at positive voltages, whereas the 6±1-MeV (B) and 10±1-MeV (C) phonons appear predominant at negative voltages. Phonon-assisted tunneling was generally weak in low-resistance units. In evaporated Bi film junctions, even though the resistance often ex-

[3] We point out that two phonon peaks at +7 and −10 mV in Unit S-65 were previously (Ref. 1) misinterpreted as being due to band edges. We also point out that the phonon structure observed here is of a quite different origin from that observed in a superconductor-oxide-normal metal tunnel junction. The latter structure is due to phonon effects in the tunneling density of states for the superconductor, rather than to the threshold associated with phonon-assisted tunneling.

[4] See, for example, R. N. Hall, in *Proceedings of International Conference on Seminconductor Physics, Prague, 1960* (Czechoslovak Academy of Science, Prague, 1961), p. 193.

[5] J. M. Rowell and W. L. McMillan, Bull. Am. Phys. Soc. **12**, 77 (1967).

[6] G. A. Antcliffe and R. T. Bate, Phys. Letters **23**, 622 (1966).

ceeded 500 KΩ, the phonon process was difficult to resolve, in contrast to the marked structure of single-crystal units. This is probably due to the larger number of single-crystal units. This is probably due to the larger number of scattering centers in poorer-quality materials. Nevertheless, every evaporated Bi junction did show weak but discernible structure at $\sim+100$ and ~-200 mV, because of the combined effect of several band edges. As the voltage applied to a polycrystalline junction was increased, further structure appeared at $+0.65$, -0.6, -0.8, and -1.6 V, as shown in the insert of Fig. 1. This structure, which may have been enhanced by the phonon process, is also believed to be caused by the onset of new bands.

Application of magnetic fields up to 84 kOe did not produce a significant change in the general characteristics. Some change near zero bias did appear, as displayed in Fig. 2 by the dashed curve for Unit 311-11 and by the curves in the insert. The effect seen here is essentially that particular phonons become dominant over others in the presence of a magnetic field because of the resultant quantization of the electron momentum.

We may use the effective-mass Hamiltonian[7] to justify our associating each phonon bump for the trigonal units with one of the four nondegenerate phonon modes in the trigonal direction. Energy conservation does not introduce any restriction on which phonons may assist the tunneling. The restriction to trigonal phonons arises from the fact that the tunneling process conserves k_t, the quasimomentum transverse to the junction plane. This conservation law results from the assumption of specular reflection and the use of the effective-mass Hamiltonian. If a Bi phonon of wave vector $\mathbf{q}$ is emitted during tunneling, then the conservation of k_t requires that $k_t(Al_2O_3)=k_t(Bi)\pm q_t\approx q_t$, since the Fermi momentum of both the electrons and the holes of Bi is very small. Oblique tunneling, i.e., $k_t(Al_2O_3)\neq 0$, is much less probable than normal tunneling, because a nonzero k_t leads to a substantial increase of the effective barrier height in the oxide, by the addition of the term $\frac{1}{2}\hbar^2k_t^2m^*$, where m^* is the effective mass in the oxide. Therefore the $q_t\approx 0$ phonons (the trigonal phonons) are much more favored for phonon-assisted tunneling. From this point of view, we would expect that a unit having a junction plane other than trigonal would show six phonon bumps. However, in no direction is the energy separation of the transverse modes[2] more than about 1 MeV. Therefore it is not surprising that we cannot distinguish between six bumps and four bumps.

To summarize, the existence of phonon-assisted tunneling in Bi tunnel junctions appears to be well established and provides a simple and accurate method for locating the band-edge energies by tunneling spectroscopy. However, a detailed analysis of the phonon process is still to be worked out.

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[7] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257. When using the effective-mass Hamiltonian, the k_t of the envelope wave function is measured from the bottom or top of each respective band. Therefore, within the framework of the effective-mass Hamiltonian, it is irrelevant that the various conduction and valence bands of Bi are located at different points in the Brillouin zone.