

then suggest that the final state of the interstitials produced by radiation at room temperature is different from that produced by irradiation at lower temperatures.<sup>8</sup>

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<sup>1</sup>W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).

<sup>2</sup>J. S. Nadeau, *J. Appl. Phys.* **34**, 2248 (1963), **35**, 1248 (1964), **33**, 3480 (1962).

<sup>3</sup>W. A. Sibley and E. Sonder, *J. Appl. Phys.* **34**, 2366 (1963).

<sup>4</sup>W. Gebhardt, *J. Phys. Chem. Solids* **23**, 1123 (1962). These samples were irradiated at low temperature. C. T. Walker [*Phys. Rev.* **132**, 1963 (1963)] has obtained similar results after room-temperature irradiation. In contrast to Gebhardt's explanation of the thermal

conductivity change to interstitials, Walker explained his results in part by assuming that *F* centers created a strain field.

<sup>5</sup>D. A. Wiegand and R. Smoluchowski, in "Actions Chimique et Biologiques des Radiations", edited by M. Haissinsky (Masson et Cie, Paris, 1964).

<sup>6</sup>Due to the intense coloring of the samples, less than one part in 10<sup>4</sup> of monochromatic *F* light penetrates as far as the center of the samples.

<sup>7</sup>For white light the I "IR No. 2" tungsten lamp of the Cary 14R spectrophotometer was used. This is the source normally used for infrared scans where the light is analyzed after it passes through the sample.

<sup>8</sup>H. Hersch has observed *F*-center bleaching effects in KI similar to those we report here. Moreover, he observed a *V* band at 3.7 eV after irradiation at dry-ice and warming to room temperature. This band is easily bleached with *F* light. Room-temperature irradiation, on the other hand, produces absorption at shorter wavelengths which is difficult to bleach. We would like to thank H. Hersch for communicating his unpublished results.

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## STUDY OF ELECTRONIC BAND STRUCTURES BY TUNNELING SPECTROSCOPY: BISMUTH

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We have observed prominent structure in the conductance ( $dI/dV$ ) versus voltage plot of the tunneling current between single-crystal Bi and an evaporated Al film. It appears that despite pessimistic forecasts,<sup>1</sup> electron tunneling can be used as an effective tool for the study of energy band structures of semimetals.

The sample was constructed of an Al<sub>2</sub>O<sub>3</sub> film several tens of angstroms thick on a cleaved surface (trigonal plane) of Bi with a counter electrode of active area about 10<sup>-4</sup> cm<sup>2</sup> of Al deposited over the oxide. The experiments were carried out at temperatures where the Al film was always a normal metal.

Figure 1 is a plot of the conductance of such a sample plotted versus voltage at 2°K (solid line). A positive voltage has the Al electrode at a higher potential than the Bi, and hence the electronic structure below the Fermi level in the Bi shows up. A negative voltage shows electronic structure above the Fermi level. There was very little change in the curve in the temperature range 2 to 4°K. At temperatures in the range 80°K, the fine structure was

absent while the general "w" shape of the curve was retained. As an approach toward interpreting the structure in Fig. 1, the curve was treated as a sum of the conductances from many hole- and electron-band edges.<sup>2</sup> Figure 2 is an illustration of this method. Here is plotted the conductance of the peak occurring at ~+37 mV. This is roughly arrived at by subtracting the actual conductance from a continuation of the "background conductance." Also in Fig. 2 is a reconstructed plot of the tunneling current versus voltage for this band.

In the above-mentioned framework we have constructed the conductance for a series of band edges which generally fit the observed conductance curve in Fig. 3. For a given sample the ratio of the peak value of the conductance to the value in the plateau is different for different bands. It was also noted that for different samples the ratio is different for the same band although the peak occurs at substantially the same voltage.

Because, at the present time, there is some uncertainty as to where to assign the band edge

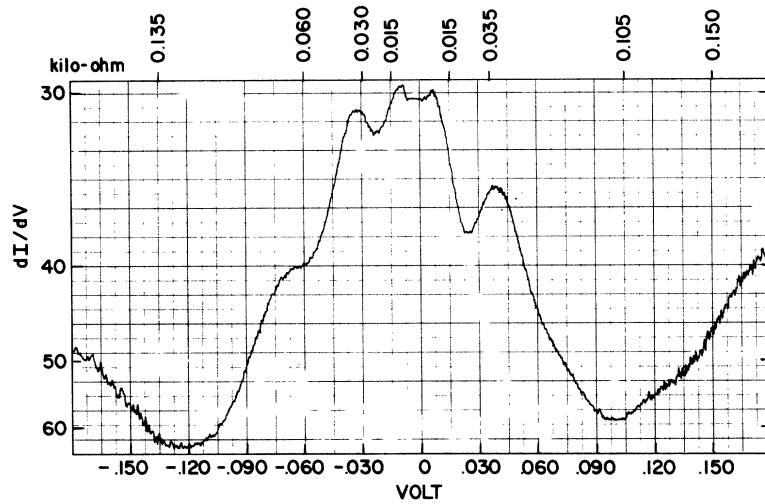


FIG. 1.  $dI/dV$  versus applied voltage for experiment.

relative to the individual conductance curve, we have arbitrarily chosen a position on the shoulder of the peak as is shown in Figs. 1 and 3. We feel that the uncertainty associated with this arbitrariness of choice is within  $\pm 5$  mV.

In Fig. 3, we show the four conduction and four valence bands we have observed. It is possible that there are other bands present in this energy range but they are not distinguishable at the present time. The positions of bands

A, B, and C are fairly well known, and the values we assign are in fairly good agreement with previous estimates as summarized in Table I. From the fact that the magnitude of the conductance of band D is comparable to that of band C and that we believe the magnitude is related to the effective mass, we have tentatively assigned band D as being the conduction band associated with valence band C.

For tunneling between simple normal metals, one would expect to see no dependence on the density of states from the independent-particle point of view in the WKB approximation. Also, from this point of view, one would expect a generally smooth curve with minor fluctuations

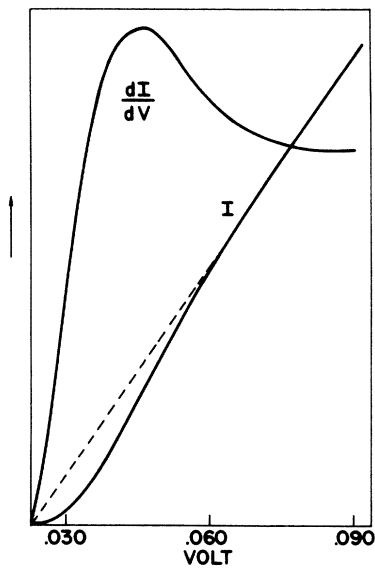


FIG. 2. Both tunneling current and its conductance versus applied voltage for a particular band. Note an anomaly near the band edge.

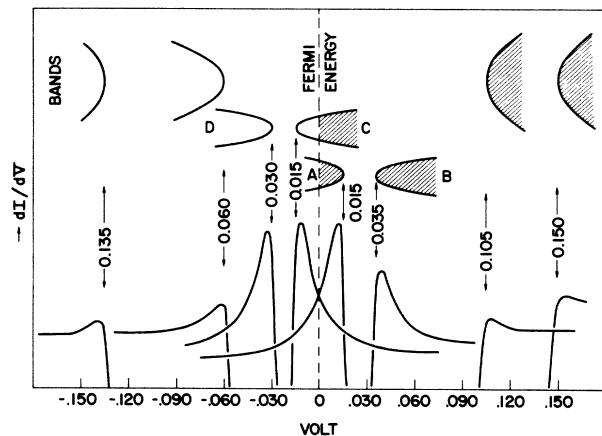


FIG. 3. A schematic illustration of each component of conductance and its related band.

Table I. Band energies in Bismuth.

References	Fermi energy (meV)		Energy gap (meV)	
	For electrons	For holes	For electron band	For hole band
a	...	...	24	...
b	25	...	15	...
c	...	12	...	...
d	27.6	11	15.3	...
e	27 for sum of both		...	...
Present work	15	15	20	15

<sup>a</sup>W. E. Engeler, Phys. Rev. 129, 1508 (1963).

<sup>b</sup>R. N. Brown, J. C. Mavroides, and B. Lax, Phys. Rev. 129, 2055 (1963).

<sup>c</sup>Y.-H. Kao, Phys. Rev. 129, 1122 (1963).

<sup>d</sup>G. E. Smith, G. A. Baraff, and J. M. Rowell, IBM J. Res. Develop. 8, 228 (1964).

<sup>e</sup>A. L. Jain and R. L. Jaggi, IBM J. Res. Develop. 8, 233 (1964).

when tunneling into a semimetal. However, the observed structure is quite large. It is felt that the WKB approximation is not applicable for semimetals and degenerate semiconductors as the electron and hole wavelengths are larger than the junction width. In fact, at a band edge, the wavelengths are extremely large in any material, and one would expect a complete breakdown of the WKB approximation at this point.

One possible explanation for the observed structure is that proposed by Harrison<sup>1</sup> for the case of the sharp boundary which illustrates a dependence of tunneling current on the one-dimensional density of states.

In this study we have detected many bands in Bi, most of which have never been seen with other experimental methods. This demonstrates

that this technique of tunneling spectroscopy has great potential for band-structure studies in semimetals and degenerate semiconductors and, in particular, in the study of the  $\text{Bi}_x\text{Sb}_{1-x}$  alloy system.

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<sup>1</sup>W. A. Harrison, Phys. Rev. 123, 85 (1961).

<sup>2</sup>M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. 8, 215 (1964). The authors find from a theoretical treatment that one would expect many bands to be located in a small energy range near the Fermi energy.

## DETECTION OF THE ac JOSEPHSON EFFECT

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Josephson<sup>1</sup> made two startling predictions in 1962 of effects which have become known as the ac and dc Josephson effects. The dc effect, which allows supercurrent to flow between the ground state of two superconductors in an electron tunneling experiment,<sup>2</sup> is now well established experimentally.<sup>3</sup> The ac effect, which allows current flow between the ground states of two superconductors when there is a small

potential difference  $V$  between them, has found only indirect experimental support.<sup>4-6</sup> This current flow is accompanied by photon emission; the frequency  $\nu$  of the photons is given by  $h\nu = 2eV$  where  $h$  is Planck's constant,  $e$  the electronic charge, and  $V$  the potential difference between the two superconductors. The frequency is related to twice the electronic charge as the two superconductors exchange

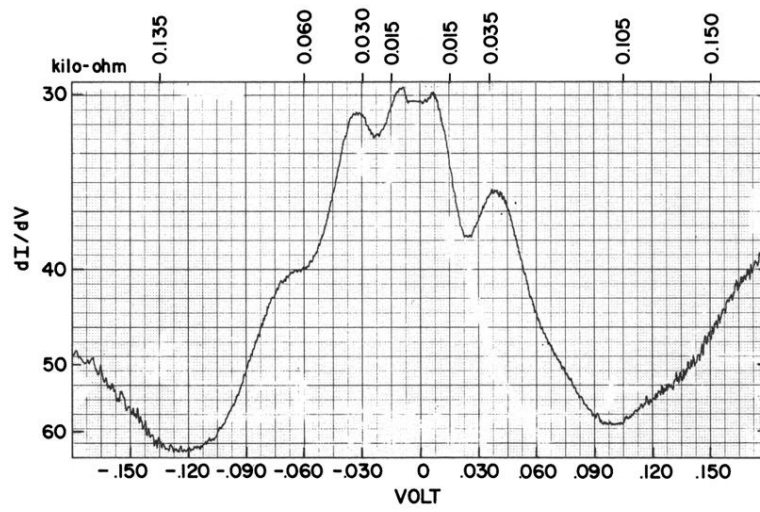


FIG. 1.  $dI/dV$  versus applied voltage for experiment.