PHYSICAL REVIEW VOLUME 76, NUMBER 2 JULY 15, 1949

Some Semimetallic Characteristics of the Photoelectric Emission from As, Sb, and Bi

L. APKER, E. TAFT, AND J. DICKEY
General Electric Research Laboratory, Schenectady, New York

(Received March 31, 1949)

Spectral and energy distributions were determined for photoelectrons from crystalline evaporated layers of As, Sb, and Bi. The relative numbers of electrons ejected from states near the Fermi level were obtained by the method of interchangeable emitters. In each case, the result was several times smaller than that expected for a simple metal. Structure was observed in the energy distribution function $N(\nu, E)$ for Sb. These effects were attributed qualitatively to an overlapping of energy bands like that assumed in the conventional model for semimetals. Data could be analyzed conveniently with the aid of the function $N(\nu, E)/E$ previously applied to semiconductors. Spectral distributions, relatively insensitive in form to deviations from metallic behavior, could be fitted by Fowler plots. Work functions so determined differed by less than 0.1 ev from the following values derived from energy measurements: As, 4.72 ev; Sb, 4.60; Bi, 4.34.

I. INTRODUCTION

PREVIOUS studies have dealt with the photoelectric emission from several elementary semiconductors.[1] The electronic energy structures of these materials had readily measurable effects on the character of both the energy and the spectral distributions of the photoelectrons. On the other hand, distribution functions for different types of metals have shown no appreciable differences in form. The emission from elements as unlike as sodium and tungsten, for instance, can be specified near the threshold by the well-known results that Fowler and DuBridge have derived from considerations of the Sommerfeld model.[2] The volume properties of the semimetals indicate that the energy structures of these substances are in an intermediate class. It is perhaps interesting to ask, then, if any clear-cut evidence of this is to be found in the external photoelectric effect. Techniques based on Millikan's method of interchangeable emitters[1] permit a convenient attack on such a problem. Results so obtained on the series As, Sb, and Bi are given in this paper.

II. EXPERIMENTAL DETAILS

The eight photo-tubes used were like those described in reference 1. Bi was investigated in three, Sb in two, and As in three. These elements were deposited from the vapor on substrates of Ni, Mo, Pt, Cb, fused quartz, graphite, or Ni-Fe alloy. Commercial grade Bi was used in one tube; all other samples were spectrographically standardized materials obtained from Johnson, Matthey Company, Ltd. They were evaporated from graphite crucibles, from Ta boats, or, in the case of As, from Pyrex distillation trains. Ionization gauges indicated pressures of $<5\times10^{-8}$ mm Hg after the seal-off except in tubes containing As; here the amorphous form of the element was present with a vapor pressure apparently of the order of 10^{-6} at 300°K. Miss Eileen Alessandrini kindly took electron diffraction data on the emitters after they had been removed from the tubes.

Because of difficulties met in working with As, complete data including electron diffraction photographs were taken on only one surface. This sample was deposited directly in crystalline form. On cool substrates, As normally condenses as a semiconducting amorphous layer.[1] Films of this type, on Ta or graphite, were heated by focused radiation from a one-kilowatt tungsten lamp. The characteristics thereupon ceased to be typical of a semiconductor and approached those described here. When the tubes were opened, the surfaces oxidized before electron diffraction data were obtained. Thus, there was no proof that the samples had crystallized, although it is reasonable to assume that this happened.[3] Results for As must be presented, therefore, as tentative. For Sb and Bi, data were checked for reproducibility on two or more surfaces in each tube. At $h\nu=5.80$ ev, the photoelectric yield varied by less than a factor of two from surface to surface and by less than 1 percent over any single surface. Neither spectral nor energy distributions showed measurable variations in form.

Other experimental details have been given previously.[1, 2]

III. DISCUSSION OF RESULTS

Current-voltage characteristics are given in Fig. 1. Overlapping is avoided by setting the curves coincident at the saturation points V_s rather than at the more significant point V_0, the "stopping potential for 0°K." (Symbols in this paper are the same as in reference 1.) The abscissa $V-V_s$ is thus equal to $-E/e$, where E is the kinetic energy of the photoelectrons after emission. Initial energies ϵ may be obtained from the equation $\mu-\epsilon=h\nu-\varphi-E$, where μ is the Fermi level. Work functions determined from the relation $\varphi=h\nu-e(V_s-V_0)$ were 4.34 ev for Bi, 4.60 for Sb, and 4.72 for As.

As shown explicitly in Fig. 1, the characteristic for Bi lies well below that for a simple metal with the same

---

[1] Apker, Taft, and Dickey, Phys. Rev. **74**, 1462 (1948); E. Taft and L. Apker, Phys. Rev. **75**, 344 (1949).

[2] Apker, Taft, and Dickey, Phys. Rev. **73**, 46 (1948), and cited papers.

[3] R. Suhrmann and W. Berndt, Zeits. f. Physik **115**, 17 (1940).

work function. Sb and As gave similar results. For all of these semimetals, therefore, the relative numbers of photoelectrons originating in states near the Fermi level were considerably smaller than for simple metals. In Fig. 2 this is also apparent from the behavior of $N(\nu, E)/E$.[4] This function, which has been of value in analyzing data on semiconductors,[1] was interpreted as being roughly proportional to $s(\nu, \epsilon)n(\epsilon)f(\epsilon)$, where s is an excitation probability, n is the density of states, and f is the Fermi factor; ϵ, as mentioned above, is the energy of the electrons before excitation. Several properties of As, Sb, and Bi have been treated with the aid of a simple model in which the valence electrons occupy two energy bands that overlap each other slightly.[5] In order of magnitude, the amount of overlap is 1 ev, and the Fermi level μ lies in this region of encroachment. Under these conditions, s and n may undergo relatively rapid variations near μ, and structures like those in Fig. 2 may result. The curves contrast strikingly with the smooth characteristics typical of semiconductors, for which n (and almost certainly s) depend monotonically on ϵ near the edge of the single band involved. By assuming that s does not depend strongly on ϵ, one may obtain the form of nf from N/E.[6] Although such an argument is probably not applicable in detail to semimetals, the density of states derived on this basis is relatively low near μ—a result to be expected from the simple model.

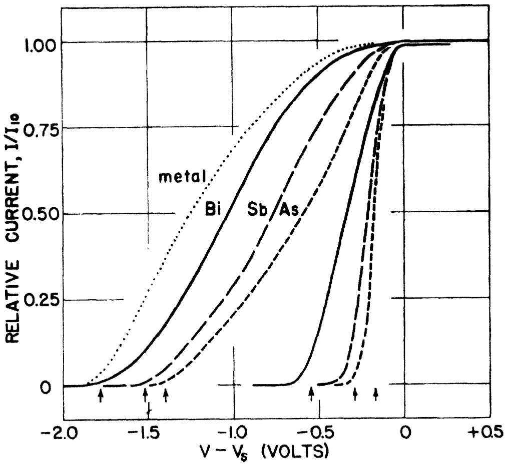

FIG. 1. Current-voltage characteristics for crystalline semimetals at 300°K. Curves are normalized with $I/I_{10}=1$ at $V=+10$ volts. Abscissas are $V-V_s$ and saturation points are coincident. For the three curves at the right, $h\nu=4.89$ ev; for the others, $h\nu=6.12$. Arrows mark values of V_0-V_s found from data on reference metals. The dotted curve is for a simple metal with $\varphi=4.34$ ev; it may be compared directly with the adjacent characteristic for Bi. Experimental errors are not visible on this scale. At $V=1000$ and $h\nu=6.12$, $I/I_{10}=1.02$ for Bi and Sb, and 1.03 for As.

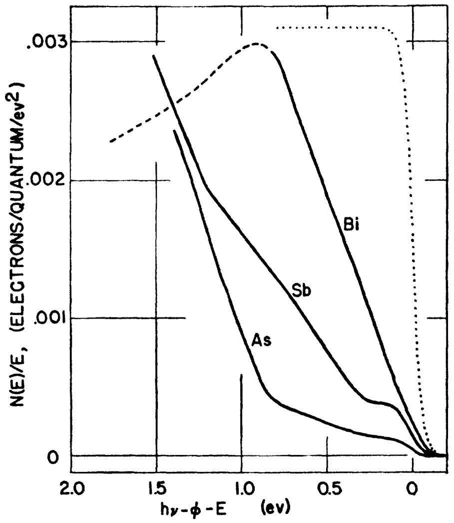

FIG. 2. $N(E)/E$ for 300°K and for $h\nu=6.12$ ev. The dashed portion of the Bi characteristic is discussed in the text. The dotted curve shows the Fermi factor (arbitrarily normalized at 0.0031), which is characteristic of a simple metal on this type of plot. For metals having the same yields as As, Sb, and Bi at $h\nu=6.12$ ev, the appropriate Fermi factors are normalized at 0.00017, 0.00043, and 0.0013, respectively.

Perhaps the most interesting feature in Fig. 2 is the plateau for Sb near $h\nu-\varphi-E\sim 0.2$ ev. While the values of N/E decreased by a factor of 1.8 as $h\nu$ increased from 5.80 to 6.71 ev, the location and shape of the plateau did not change. One concludes that the form of $s(\nu, \epsilon)$ did not depend on ν, and that two groups of initial energy states having dissimilar properties were separated by the point $h\nu-\varphi-E=\mu-\epsilon\sim 0.3$ ev. If the bottom of the upper band had this location, nf would have a form somewhat like that shown in the figure.

It is interesting also that the curve for Bi has a maximum. This peak shifted from $h\nu-\varphi-E\sim 0.7$ to 0.9 ev as $h\nu$ varied from 5.42 to 6.12 ev; at $h\nu=6.71$, it disappeared but a plateau was still evident. To indicate the variable portion of the curve, a dashed line is used in the figure. It should be noted that when E falls below a few tenths of an electron volt, the process of determining N/E is no longer reliable. (The curves shown are terminated at the point for which $E=0$.) Experimental errors in E may become appreciable, and patch fields due to surface non-uniformity may produce effects like those just described.[1] For these reasons, we attach less

---

[4] Here N is the energy distribution function. To make a quantitative comparison, one may contrast the semimetals with simple metals having the same yields at $h\nu=6.12$ ev. Then at $h\nu-\varphi-E=0$, the value of N/E for the semimetals is lower by a factor of about two than N/E for the metals. If the semimetals are compared with metals having the same N/E at $h\nu-\varphi-E=1.0$ ev, the discrepancies at the Fermi level are even larger.

[5] For references and discussion, see Frederick Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company Inc., New York, 1940); A. H. Wilson, *Semi-Conductors and Metals* (Cambridge University Press, London, 1939); N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936). For recent work on Sb, see S. H. Browne and C. T. Lane, Phys. Rev. **60**, 895 (1941); K. Rausch, Ann. d. Physik **6**, 190 (1947).

[6] For metals, of course, this is known to be justified; moreover, n is nearly constant and the result is practically identical with f as shown by the dotted curve in Fig. 2. When the top of the occupied band of a semiconductor is a few tenths of an electron volt below μ, f is so nearly unity at 300°K that it need not appear explicitly.

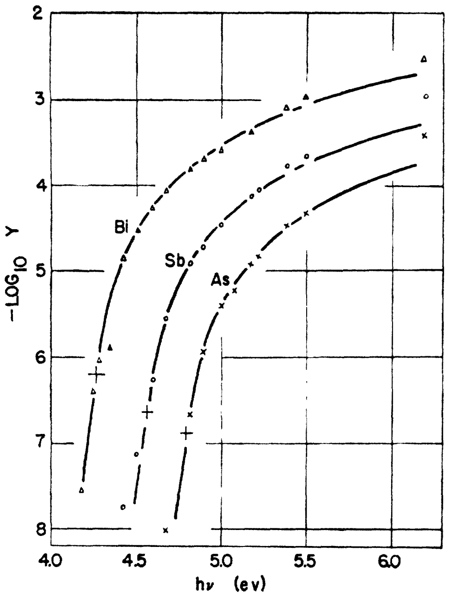

FIG. 3. Spectral distribution of the yield Y (in electrons/quantum) at 300°K. Curves through the experimental points are computed from Fowler's equation. Work functions determined from these plots are: Bi, 4.26 ev; Sb, 4.56; As, 4.79.

significance to the maximum for Bi than to the plateau for Sb.[7] The solid portion of the curve for Bi, however, should be trustworthy.

Thus, the photoelectric energy distributions given here for As, Sb, and Bi show evidence of irregular initial energy spectra. In contrast, no such effect is observable in the spectral distributions of Fig. 3. For all three semimetals, the results may be fitted within experimental error by Fowler plots. The data for Bi are in excellent agreement with previous work by Jupnik.[8] The work function found for Bi by this method is lower than that obtained from energy data by almost 0.1 ev. For Sb and As, the discrepancies are smaller and doubtless not significant.

It is not surprising, of course, that spectral distributions are comparatively insensitive to deviations from metallic behavior. Such deviations show up directly in the energy distributions, but appear only in integrated form in spectral data. In the latter case, too, the effects may be distorted by the dependence of s on ν. Further, the experimental errors in measured radiation intensities are large compared to those in current-voltage characteristics. This is reflected in the scatter shown by spectral data even when they are plotted logarithmically.

The semimetals become relatively close-packed on melting, and irregularities due to their unusual crystal structures disappear.[9] Hence, the energy distributions given here should become metallic in character when the materials liquefy. Gallium, which may also show this effect, is particularly interesting from an experimental point of view since it has a convenient melting point and a low vapor pressure.

---

[7] One may speculate about another result also affected, perhaps, by the uncertainties associated with small values of E: In the order Bi to As, the curves in Fig. 2 exhibit progressively wider regions in which N/E is relatively low. This is consistent with the increasing energy gaps expected at the boundaries of the important Brillouin zones (reference 5).

[8] H. Jupnik, Phys. Rev. **60**, 884 (1941).

[9] N. F. Mott, Proc. Roy. Soc. **A146**, 465 (1934); see also reference 5.