Structure in the Energy Distribution of Photoelectrons from K_3Sb and Cs_3Sb

E. A. TAFT AND H. R. PHILIPP
General Electric Research Laboratory, Schenectady, New York
(Received April 27, 1959)

The energy distributions of photoelectrons from K_3Sb and Cs_3Sb show structure that is similar in form to structure in the spectral dependence of the optical absorption. One may rationalize this empirical result by saying that both the photoelectric and optical effects arise from structure in the state density of the valence band. Assuming that the optical absorption involves transitions to the conduction band, a lower limit for the electron affinity of the crystal is 0.6 ev for K_3Sb and 0.4 ev for Cs_3Sb.

INTRODUCTION

THE semiconductor Cs_3Sb is a well-known photoemitter. Following the initial work of Görlich in 1936, it has been the subject of extensive research.[1] As a result, its salient properties are rather well known. They are outlined in a recent paper by Spicer.[2] Spicer also investigated (among other materials) the closely related compound K_3Sb and found pronounced structure in the spectral dependence of the optical absorption.

The present report describes further work on these substances. The spectral dependence of the optical absorption is compared in detail with photoelectron energy distributions at $\sim$300°K and $\sim$90°K. The optical and photoelectric results bear a surprising resemblance to each other. We speculate that this may be a result of structure in the density of states of the valence band. On this basis, it is possible to deduce a lower limit for the electron affinity of the crystal. In addition, for Cs_3Sb, one particular peak which appears at $h\nu\sim2.25$ ev (in both the optical absorption and in the photoelectric yield) behaves in a very different way from the others. This result supports a previous conclusion by Borzyak[3,4] that this feature is due to exciton formation.

EXPERIMENTAL DETAILS

Previous papers describe the kind of phototube used in this work.[5,6] It was a very simple type, in which a small emitter disk was mounted inside a cylindrical collector closed at both ends. Energy distributions were measured by the usual retarding potential techniques. Despite the departure from the customary concentric-sphere design, these tubes are surprisingly trustworthy for energy distribution experiments. In tubes designed for more precise work, the effects described in this paper should be even more pronounced.

Optical absorption data were obtained on films (or wedges) of various thicknesses formed on the inside of tubes made of fused silica. In many cases, optical data were also obtained on deposits formed on the Nonex glass phototube envelopes. Very rough estimates of the thickness of K_3Sb deposits were made by evaporating weighed amounts of Sb in a known geometry. Thus, the magnitude of the absorption constant for K_3Sb could be assessed in a crude way. For Cs_3Sb, only relative magnitudes of the absorption constant were determined. It was then assumed that the absorption constant at $h\nu=2$ ev was 10^5 cm^{-1} in agreement with previous determinations.[1,7,8] Magnitudes at other photon energies were thus evaluated.

The compounds were formed as outlined in Spicer's paper[2] and in the references cited there. Both optical and photoelectric data were obtained near 90°K by cooling the entire tube in a copper enclosure mounted in a Dewar vessel with suitable windows.

RESULTS AND DISCUSSION

Figure 1 shows the optical absorption of K_3Sb at $\sim$300°K. There is a pronounced peak near 2.4 ev, a minimum near 3.0 ev, and another maximum near 3.4 ev. These features are substantially the same as those in Spicer's data (although they may occur at

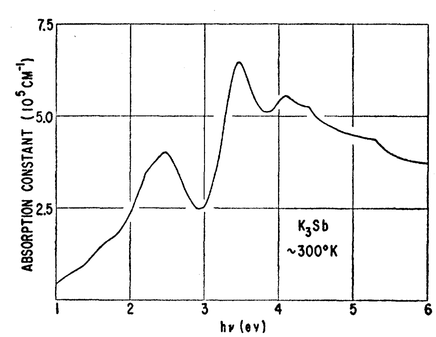

FIG. 1. Optical absorption of K_3Sb. Absolute magnitudes were estimated as described in the text.

[1] See G. Wallis, Ann. Physik **17**, 401 (1956), and cited references.
[2] W. E. Spicer, Phys. Rev. **112**, 114 (1958), and cited references. See also P. G. Borzyak, Trudy Inst. Fiz. Akad. Nauk Ukr. S.S.R. **2**, 16 (1952).
[3] P. G. Borzyak, Trudy Inst. Fiz. Akad. Nauk Ukr. S.S.R. **4**, 28 (1953). See also, H. Miyazawa, J. Phys. Soc. (Japan) **8**, 169 (1953).
[4] Yu. K. Shalabutov and N. S. Maslenikova, Zhur Tekh. Fiz. **26**, 1166 (1956) [translation: Soviet Phys. Tech. Phys. **1**, 1137 (1957)].
[5] Apker, Taft, and Dickey, J. Opt. Soc. Am. **43**, 78 (1953); Taft, Philipp, and Apker, Phys. Rev. **110**, 876 (1958).
[6] E. Taft and L. Apker, J. Opt. Soc. Am. **43**, 81 (1953).
[7] Morgulis, Borzyak, and Dyatlovitskaya, Izvest. Akad. Nauk **12**, 126 (1948).
[8] J. A. Burton, Phys. Rev. **72**, 531(A) (1947). For data see V. K. Zworykin and E. G. Ramberg, *Photoelectricity and Its Application* (John Wiley & Sons, Inc., New York, 1949).

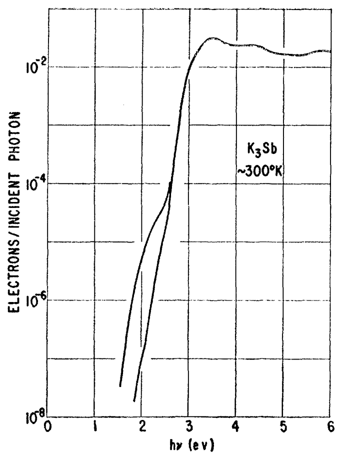

FIG. 2. Spectral distribution of the photoelectric yield for two different samples of K_3Sb.

slightly different values of $h\nu$). Very weak inflections near 1.3 ev and 1.85 ev appear to us tentatively to be reproducible. They agree with the data points in Spicer's Fig. 1.[2] Further, the first strong peak appears to be double, with the weaker component near 2.2 ev. Other structure occurs in the region beyond 3.5 ev. Among these various features in the absorption, we shall be most interested in the strong double peak near 2.4 ev.

Figure 2 shows the spectral distribution of the photoelectric yield from two different K_3Sb surfaces. Response in the threshold region is not reproducible among different samples, apparently because of the influence of excess K.[2] In the plateau region, however, the yield is much more reproducible. It becomes maximum at about the same points as does the optical absorption.

Figure 3 shows photoelectron energy distributions for several values of $h\nu$. When $h\nu=6.38$ ev, a major fraction of the electrons have low energies. An effect of this kind has previously been ascribed (in the case of Cs_3Sb) to scattering of excited electrons by electrons in the valence band, a process which apparently is important at this value of $h\nu$.[5,6,9] In spite of this, three weak but reproducible peaks appear in the energy distribution near energies $E=1.8$, 2.5, and 3.4 ev, respectively. This part of the distribution, especially the two peaks of higher energy, is composed of electrons that have not been involved in the strong scattering process mentioned above.

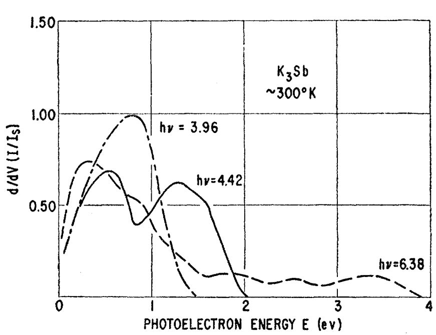

FIG. 3. Normalized energy distributions for photoelectrons from K_3Sb. These were obtained by differentiating current-voltage characteristics.[5,6] Estimated errors in ordinates are below 10% for abscissa above 1 ev. The features shown have been reproduced in more than ten samples.

It is conceivable that these peaks arise from structure in the state density of the valence band of K_3Sb. If this is correct, the energy distribution for $h\nu=4.42$ ev should show the same kind of effect, but with the peaks shifted by an amount equal to the difference in the photon energies. The data appear to follow this pattern. For $h\nu=4.42$ ev, the peak of highest energy, with its characteristic double form, appears near 1.4 ev—approximately the expected position.

We may also ask if this structure can be correlated with structure in the optical absorption. Figure 4 is arranged to throw light on this question. Consider first

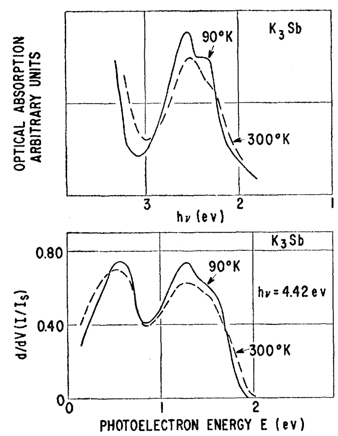

FIG. 4. Optical absorption and photoelectron energy distributions for K_3Sb. The abscissa scales arranged with $E+h\nu=4.42-\alpha=3.85$ ev as described in the text. (The zero point on the ordinate scale for optical absorption is shifted.)

a photon of energy $h\nu$ which is involved in the following optical absorption process: namely, the excitation of an electron from a given initial state in the valence band to a final state (in the conduction band) which lies at an energy below the vacuum level by an amount α. Also, consider the kinetic energy E of an external photoelectron ejected from the same initial state by a

[9] In Si, an electron must have an energy near 2.25 ev *in* the conduction band before it can make an inelastic collision with an electron in the valence band and produce an electron-hole pair [A. G. Chynoweth and K. G. McKay, Phys. Rev. **108**, 29 (1957)]. Thus, the threshold energy for pair production by electrons is about twice the forbidden band gap (the energy at which the process is just possible energetically). One concludes that important restrictions are imposed by momentum conservation [P. A. Wolff, Phys. Rev. **95**, 1415 (1954)]. In reference 5, data for Cs_3Sb showed that strong scattering, attributed there to pair production, apparently set in only a little above the energy at which it became energetically possible. This is surprising, especially in view of the results for Si. It may be pertinent, however, that Cs_3Sb has a disordered lattice [K. H. Jack and M. M. Wachtel, Proc. Roy. Soc. (London) **A239**, 46 (1957)]. This disorder, along with other defects in these films, may break down the stringent momentum restrictions generally expected for a more perfect crystal.

photon of energy 4.42 ev, the value used in Fig. 4. The photon energy $h\nu$ involved in the optical process will lie directly above the photoelectron energy E in Fig. 4 if the abscissa scales are arranged so that $E+h\nu=4.42-\alpha$.

Now, in this diagram, a peak in the state-density of the valence band will produce a related and similar structure in the optical absorption only if the optical transitions take place to a single final state (or a narrow group of states) of the type just mentioned (and if the transition probability does not vary rapidly with the energy of the initial state).

A related and similar structure will also appear in the energy distribution of the photoelectrons if both the escape probability for excited electrons and the photoelectric transition probability do not vary rapidly with energy. Clearly, it would be surprising if these conditions were satisfied in any accurate way. However, if α is adjusted to 0.6 ev in Fig. 4, the structures which appear, one above the other, are very similar. Further, near 90°K, the components of the double peak apparently sharpen and become better resolved, the effect being somewhat more pronounced in the optical results than in the photoelectric. The value of α given above is determined from the data for 90°K. Thus, we can make a consistent picture of these results by saying that there are rather sharp peaks in the state-density of the occupied energy band, and that similar structure in the optical absorption is due to transitions to an effective level (or narrow group of levels) lying at an energy $\alpha\sim0.6$ ev below the vacuum level. For reasons discussed at greater length below, we consider it improbable that this effective level lie below the bottom of the conduction band, since it would then be associated with defects. Accordingly, in this rationalization, $\alpha\sim0.6$ ev is a lower limit to the electron affinity of K_3Sb. This does not disagree with the range of values 1.1 to 1.8 ev obtained by Spicer from an approximate comparison of photoelectric, photoconductive, and optical absorption thresholds.[2]

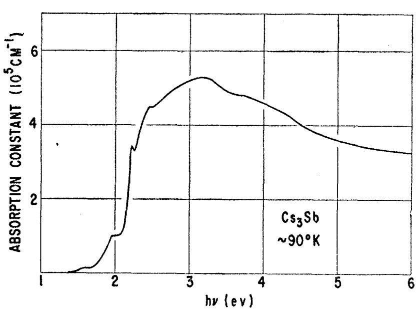

FIG. 5. Optical absorption of Cs_3Sb. Absolute values were fixed by setting the absorption constant equal to 10^5 cm^{-1} at $h\nu=2$ ev; see text.

The absolute values given for the optical absorption constant of K_3Sb in Fig. 1 are estimated only in order of magnitude. Nevertheless, they are so high that one associates them with the behavior of the bulk material rather than with defects present in small concentration. This is consistent with the reproducibility of the peak structure, as pointed out by Spicer in reference 2. Thus, we consider that these phenomena arise from properties of the K_3Sb lattice as produced by these techniques.

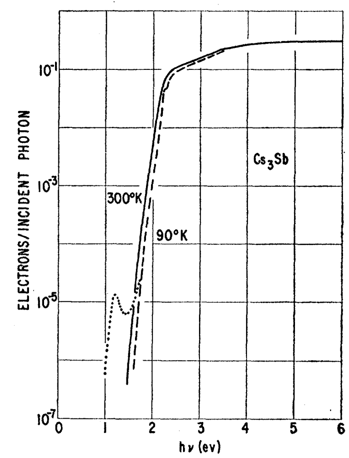

FIG. 6. Spectral distributions of the photoelectric yield from Cs_3Sb.

We turn now to the results for Cs_3Sb. The optical absorption near 90°K is shown in Fig. 5. Maxima or short plateau structures are visible at $h\nu\sim1.6$, 2.0, 2.25, and 2.45 ev. (The peak near 1.6 ev shows up in the data of Wallis.[1]) A broad peak appears near 3.2 ev, with very weak structure beyond. Figure 6 shows the spectral distribution of the photoelectric yield from Cs_3Sb at 90°K. (The peak at 1.2 ev on the curve for 90°K changes in height according to the previous irradiation of the emitter at higher $h\nu$; it is apparently associated with electrons in metastable traps; under irradiation at 1.2 ev it disappears as shown in the alternative curve with a threshold near 1.6 ev.)

Near 2.25 ev, there is a small sharp peak in the yield at 90°K. It is associated with a peak at the same energy in the optical absorption, as shown in Fig. 5. This feature has been discussed in previous work by

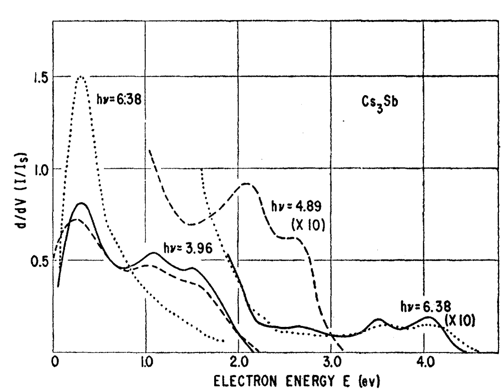

FIG. 7. Normalized energy distributions for photoelectrons from Cs_3Sb at 300°K (broken lines) and at $\sim$90°K (solid lines). For other comments see caption Fig. 3.

Borzyak,[3] who ascribed it to exciton formation. His conclusion is supported by the results given below.

Figure 7 shows energy distributions for photoelectrons from Cs_3Sb at several different photon energies. At $h\nu = 6.38$ ev, there is a predominance of slow electrons. As in the case of K_3Sb, we think this is due to electron-electron scattering processes which become important when $h\nu$ exceeds a value somewhere near 4 ev.[9] In spite of this, there appear in all the energy distributions two peaks separated by roughly 0.4 ev or a little more. At $h\nu = 3.96$ ev they are located at electron energies of about 1.1 and 1.5 ev. At $h\nu = 6.38$ ev, they appear at correspondingly shifted positions near 3.5 and 4 ev. The magnitudes of these peaks have not been determined or understood with any precision in this work. Qualitatively, however, we have never found them absent. They appear, for example, in older data,[5] although no attention was focused on them at that time.

We now follow the argument used for the more pronounced structure in K_3Sb. We associate the two peaks of highest energy in the energy distributions for Cs_3Sb with the features in the optical absorption at about 2 and 2.4 ev, respectively. It is conceivable that a third peak, which shows up at an energy near 2.7 ev on the curve for $h\nu = 6.38$ ev in Fig. 7, is related to the broad peak near 3.2 ev in the optical absorption of Cs_3Sb in Fig. 5. Correlating these features in this way, we arrive at a value near 0.4 ev (with an uncertainty of order 0.1 ev) for α, the lower limit to the electron affinity of Cs_3Sb. This is consistent with Spicer's value of 0.45 ev for the electron affinity, based on an approximation that assumed a more simple band structure.

In the energy distributions, there is no indication of similar structure corresponding to the sharp absorption peak found by Borzyak.[3] This is in accord with Borzyak's interpretation of the peak as due to formation of excitons, which may also stimulate photoemission from defects. This kind of process generally gives rise to photoelectrons that are very slow as compared with those ejected directly by photons. A slow group of this kind has been reported for Cs_3Sb.[4]

An interesting feature of this peak is that it lies between the peaks at 2 and 2.4 ev. These latter features we have assigned to structure in the valence band. Thus, the peak at 2.25 ev is above the threshold for band-to-band absorption. For the resulting excitons there is no energy restriction on dissociation, a process which may then compete with exciton stimulation of defects.[10]

CONCLUDING REMARKS

The principal result given here is empirical. There are clearly detectable peaks in the energy distributions of photoelectrons from K_3Sb and Cs_3Sb. They seem to correlate with peaks in the optical absorption. A lower limit for the electron affinity of the crystal may be deduced if the effects are assumed to arise directly from structure in the state-density of the valence band. Values so obtained are consistent with previous estimates. In the case of Cs_3Sb, an absorption peak previously found by Borzyak behaves in a distinctly different way. This is consistent with Borzyak's interpretation of this feature as an exciton peak.

There are many questions left unanswered in the present paper. The detailed origin of the peaks and their temperature dependence are interesting points for future investigation. The very close similarity in form between optical absorption and photoelectron energy distribution spectra is surprising, and it is not understood in detail. We have seen similar phenomena in other crystals, including Cs_3Bi, Rb_3Bi, Rb_3Sb, and alkali tellurides such as Cs_2Te.[6] Structure, apparently in the valence band, includes peaks like those discussed here. In these other compounds, also, the peaks are often less than 1 ev in width. Since the electronic energy structures of these materials are not known in any detail, however, further interpretation is not easy. We conclude merely that the valence bands of these materials are complex and that photoelectric methods are of interest for detecting structure in the density of states. An interesting possibility is that photoelectron energy distributions may give interpretable results on other compounds for which the band structures are better understood. Among these other crystals, we consider the alkali halides interesting.

ACKNOWLEDGMENT

We are indebted to Dr. L. Apker for many helpful discussions throughout the course of this work.

[10] A somewhat similar situation occurs in BaO. See H. R. Philipp, Phys. Rev. **107**, 687 (1957); Taft, Philipp, and Apker, Phys. Rev. **113**, 156 (1959).