

the ESR spectrum of Gd^{3+} in CaF_2 under applied stress²⁰ indicates the $4f$ electrons interact more strongly with the crystalline field than usually assumed.

For the $LaBr_3$ lattice the b_4^0 term is approximately $\frac{1}{3}$ of the b_2^0 term at room temperature, while at $77^\circ K$ this ratio changes to $\frac{1}{4}$, resulting in the unusual crossing of the lines at $H \parallel Z$ noted previously (Fig. 4). The energy levels as a function of magnetic field are illustrated in Fig. 5 (room temperature) and Fig. 6 ($77^\circ K$) for $H \parallel Z$. The b_4^0 term elevates the $\pm\frac{1}{2}$ doublet at zero field so that it is not the ground-state doublet, and the temperature variation of the b_2^0 term changes the ordering of the zero-field splitting between room temperature and $77^\circ K$. An interesting point is noted for the $H \perp Z$ direction. Upon transformation of the crystal, field terms through 90° , the b_2^0 term is effectively multiplied by $-\frac{1}{2}$ and the b_4^0 term by $+\frac{3}{8}$. The two terms which were effectively competing against each other for $H \parallel Z$ [see Eq. (3)] now add. There is

²⁰ C. M. Bowden, *Bull. Am. Phys. Soc.* **11**, 834 (1966); C. M. Bowden, Doctoral dissertation, Clemson University, 1967 (unpublished).

no longer any change in the relative positions of the lines between room temperature and $77^\circ K$ for $H \perp Z$ (Fig. 7).

We agree with the angular variation of the lines reported by Johnston, Wong, and Stafsudd⁴ for $77^\circ K$ and lower, but not at room temperature near $H \parallel Z$, where the curves are different. Further, our labelling of the transitions is different. Our use of a superheterodyne spectrometer (allowing operation at very low power levels) avoided saturation effects which would have confused the relative intensities. The peculiar ordering of the gadolinium doublets at zero magnetic field (Figs. 5 and 6) in $LaBr_3$ [with the same symmetry as $LaCl_3$ and $La(C_2H_5SO_4)_3 \cdot 9H_2O$] is further evidence that the simple point-charge model must be modified to include at least some information about the nearest-neighbor anions.

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Photoelectric Emission from Barium Telluride*

FRANK E. MARTIN† AND EUGENE B. HENSLEY

Department of Physics, University of Missouri, Columbia, Missouri

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The photoelectric emission from barium telluride has been investigated by measuring the total photoelectric-yield spectra and the distributions in kinetic energy of the emitted electrons, using a magnetic velocity-analyzer tube. From the threshold for photoelectric emission from the valence band, the energy of the top of the valence band was estimated to be 4.8 eV below the vacuum level. Using an estimate of 3.4 eV for the band gap, the electron affinity was estimated to be 1.4 eV. The kinetic-energy distributions showed two peaks which were interpreted as being associated with direct ionization of defect levels located approximately 2.9 and 3.6 eV below the vacuum level. At photon energies above about 4.1 eV, these fast peaks were observed to become distorted. This was attributed to an inelastic scattering of the electrons from the fast-peak distributions to lower kinetic energies as a result of large densities of electrons being excited to the conduction band. No evidence was seen for an exciton-induced component in the photoelectric emission.

I. INTRODUCTION

AS part of a general study of the electronic structure of the alkaline-earth chalcogenides being carried out in this laboratory, BaTe has been singled out for special emphasis.¹⁻³ In the present investigation both the total photoelectric yield and the kinetic-energy distributions of the emitted electrons from BaTe were studied. The experimental techniques used were similar

to those employed by Phillip⁴ and by Dueker and Hensley.⁵

II. EXPERIMENTAL PROCEDURE

The kinetic-energy distributions of the electrons in the photoelectric emission were measured with a magnetic velocity-analyzer tube. A schematic diagram showing the cross section of this tube is shown in Fig. 1. The envelope was a 45-mm Pyrex tube with three side arms for the cathode and collector presses and the fused quartz window. The analyzer chamber was a rectangular tantalum box containing three slits, 1.0 cm

* Supported in part by the U.S. Office of Naval Research.

† Present address: Central Missouri State College, Warrensburg, Missouri.

¹ G. J. Lapeyre and E. B. Hensley, *J. Appl. Phys.* **36**, 2054 (1965).

² H. M. Brown and E. B. Hensley, *J. Appl. Phys.* **37**, 2874 (1966).

³ C. Y. Hu and E. B. Hensley, *Bull. Am. Phys. Soc.* **10**, 386 (1965).

⁴ H. R. Phillip, *Phys. Rev.* **107**, 687 (1957).

⁵ J. E. Dueker and E. B. Hensley, *Phys. Rev.* **136**, A190 (1964).

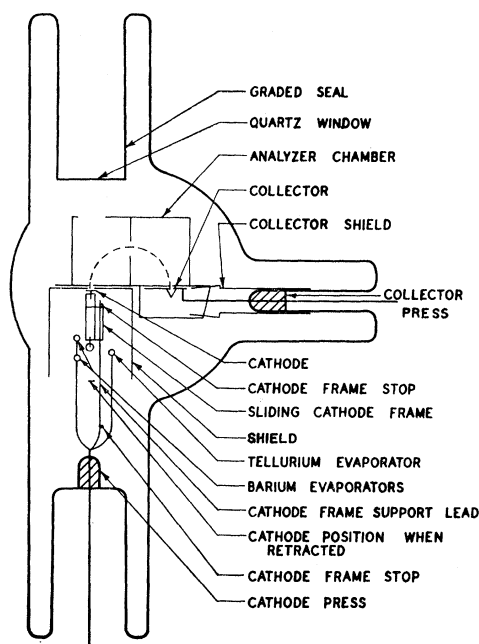


Fig. 1. Schematic drawing of the magnetic velocity-analyzer tube.

high, defining a semicircular orbit 3 cm in diam. The entrance and exit slits were 0.6 mm wide and the middle slit was 6 mm wide. This analyzer was mounted on a press perpendicular to the plane of the drawing. The electrons were deflected by a magnetic field perpendicular to the plane shown, produced by a pair of Helmholtz coils. The cathode, consisting of a thin film of BaTe on a 0.001-in.-thick, 2-mm \times 20-mm platinum ribbon, was enclosed by a cylindrical shield and could be positioned close to the slit in this shield or could be retracted to facilitate the deposition of the sample. It could be heated by passing current through it.

To obtain the kinetic-energy distributions of the photoelectric emission, monochromatic light was allowed to enter the tube through the fused quartz window, and to pass through an aperture in the analyzing chamber and through the pair of entrance slits of the analyzer to the cathode. The emitted electrons were accelerated by a known potential between the cathode and the entrance slit. The potential of the shield slit was maintained constant relative to the cathode. The current in the Helmholtz coils was adjusted to produce a magnetic field, corrected for the vertical component of the earth's field, such that electrons with a kinetic energy of 6.0 eV would traverse the slits to the collector. The kinetic-energy distributions were scanned by varying the accelerating potential.

In order to minimize enhancement effects resulting from prolonged irradiation, the data were taken using a fixed measurement cycle controlled by a timing cam. A solenoid-operated shutter was set to open for 7 sec

for each measurement and to close for 23 sec between measurements. During the shutter-closed period, the accelerating voltage was automatically advanced in approximately 0.05-V steps.

The barium telluride photocathodes were formed by depositing the elements on the heated cathode substrate. The elements were deposited with the cathode in its retracted position. The barium evaporators consisted of Kermit KIC getters. The tellurium evaporators were constructed from 0.001-in. sheet tantalum rolled into a cylinder about 5 cm long and 2 mm in diam filled with tellurium granules. When heated, the tellurium was allowed to evaporate through the overlap formed in the rolling process. Both sets of evaporators faced away from the analyzer toward the cathode in its retracted position.

The initial cathode was formed prior to sealing the tube from the vacuum system. The platinum substrate was outgassed at 1200°C and then reduced to 800°C. The tellurium evaporator was outgassed at slightly less than red-heat temperature and left at that temperature while the barium evaporators were outgassed at dull red heat. Barium and tellurium were then evaporated onto the hot cathode substrate, where they reacted to form barium telluride. After the tube was sealed off, increased activity of the cathode was obtained by evaporating barium onto the surface and annealing the film at about 400°C. Decreased activity was obtained by evaporating tellurium onto its surface and annealing.

Total photoelectric-yield data were obtained by measuring the total current to the analyzers as a function of the photon energy. Data were also obtained using simple diode tubes without the velocity analyzer. Again, in order to minimize enhancement effects resulting from prolonged irradiation, the data were taken using a fixed measurement cycle. The solenoid-operated shutter was set to open for 15 sec for each measurement and to close for 45 sec between measurements. During this 45 sec, the Gaertner quartz prism monochromator was set to the next wavelength, the focusing mirror shifted to direct the light to a calibrated photocell, and, with the shutter opened manually, the intensity was adjusted to a constant value by adjusting the width of the exit slit.

III. RESULTS

Total photoelectric-yield data for a barium telluride cathode in three different states of activation are shown in Fig. 2. The upper curve was obtained with the cathode in its most active state, which for this cathode was its as-prepared state. The intermediate curve was obtained from the cathode in a moderately active state obtained by successive evaporations of tellurium onto the cathode surface followed by periods of annealing at temperatures between 300 and 500°C. The lower curve was obtained from a highly inactive cathode obtained by continuing the deactivation process.

The thermionic effective work functions of the first two curves measured at 800°K were 2.64 and 3.78 eV, respectively. No work-function measurement was made for the inactive state because the measuring process would result in partial reactivation of the cathode.

Kinetic-energy distributions for a highly active cathode are shown in Fig. 3, and for a less active cathode in Fig. 4. The partial photoelectric yield in electrons per quantum as measured at the collector of the magnetic velocity-analyzer tube is plotted as a function of the kinetic energy for a series of photon energies from 2.8 to 5.8 eV. No attempt to reduce this to the absolute differential yield in electrons per quantum per electron volt of kinetic energy was made because the band pass of the analyzer was not accurately known. The number

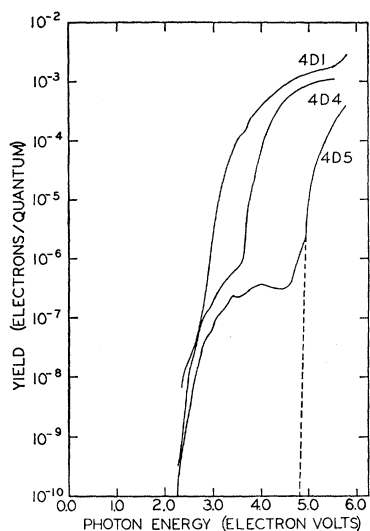


FIG. 2. Spectral distribution of the total photoelectric yield from a BaTe cathode in three different states of activation. A simple diode tube was used in obtaining these data. The thermionic effective work function measured at 800°K was 2.64 eV for 4D1 and 3.78 eV for 4D4. No work-function measurement was made for 4D5 because the measuring process would result in reactivation of the cathode.

at the lower right of each curve represents the photon energy used in obtaining that curve. Each peak is marked with the difference between the photon energy and the kinetic energy of the peak. These values should represent the median depth of the donor involved relative to the vacuum level. The zero for the kinetic-energy distributions was obtained by observing the thermionic-emission distributions.⁴

Attempts were made to obtain kinetic-energy distributions for cathodes in very low states of activation, such as 4D5 in Fig. 2. However, collector current could be measured only for photon energies near 5.17 eV. At lower photon energies the total yield was too low and at higher photon energies the available light intensities were too low. At a photon energy of 5.17 eV, a weak kinetic-energy distribution was observed

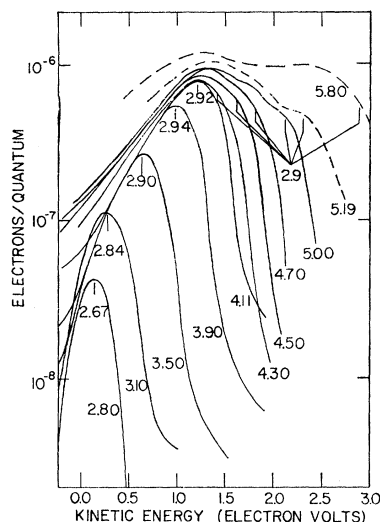


FIG. 3. Kinetic-energy distributions of photoelectric emission from a BaTe cathode in a high state of activation. The thermionic effective work function at 800°K was 2.4 eV. The partial photoelectric yield in electrons per quantum as measured at the collector (proportional to differential yield) is plotted as a function of the kinetic energy. The photon energy in electron volts used in obtaining each curve is marked at the lower right. The peaks are marked with the difference between the photon energy and the value of the kinetic energy at the peak. The light intensity for the two dashed curves was too low to give accurate data.

between 0 and 0.5 eV. The peak collector current was about 1.8×10^{-7} electrons per quantum. Although the actual collector current was too low to reveal any structural details in the distribution, the curves were consistent for electrons originating from the top of a valence band 4.8 eV below the vacuum level.

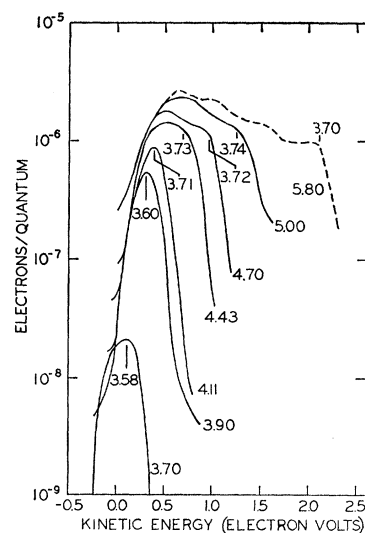


FIG. 4. Kinetic-energy distributions from a BaTe cathode in a moderate state of activation. The thermionic effective work function at 800°K was 2.75 eV. Curves are marked as in Fig. 3.

IV. DISCUSSION

The total photoelectric yield below 4.8 eV is interpreted as originating from the direct ionization of donors. Details of this interpretation will be discussed later in this section. In Fig. 2 it is observed that the yield to the right of 4.8 eV remains high even for highly deactivated cathodes. This contribution to the yield is attributed to direct transitions of electrons from the valence band. The threshold for these transitions was estimated by extrapolating the curves as shown by the dashed line. From these and similar data, it is estimated that the difference in energy from the top of the valence band to the vacuum level for barium telluride is about 4.8 eV.

An estimate of the electron affinity can be obtained from the difference between the above threshold energy for emission from the valence band and the band gap. Direct measurement of the band gap is difficult because of the masking of the band-to-band transitions by the exciton absorptions. However, for those alkali halides and alkaline-earth chalcogenides for which the band gap has been estimated, it usually lies at an energy 5 to 15% greater than the first prominent exciton absorption. The first exciton peak in BaTe is observed to be 3.1 eV.^{6,7} Hence, a good estimate of the band gap for BaTe would be about 10% larger or about 3.4 eV. Subtracting this from 4.8 eV, the threshold for valence-band emission, leads to an estimate for the electron affinity of 1.4 eV. This is in good agreement with the value of 1.5 ± 0.2 eV obtained from an analysis of thermionic emission measurements² and 1.5 eV obtained from the temperature dependence of the ratio of thermionic emission to the electrical conductivity.³

Two assumptions are implicit in the above discussion as well as in the discussion that follows. These are (a) that any effects of band bending are negligible and (b) that changes in activation do not alter the dipole layers at the surface. The much shorter mean free paths of electrons in broad band, polar insulators compared with the semiconductors in which band bending is commonly observed suggests that band bending should be less of a problem here. Also, the ease with which the work function can be changed by activation argues against the presence of surface states which could contribute to band bending. However, probably the best evidence against any measurable effects due to band bending lies in the above good agreement obtained for the electron affinity compared with alternative determinations. Direct evidence that the surface dipole layers do not change with the activation processes used here has been obtained by Hu and Hensley.³ They observed that the electron affinities of the barium chalcogenides, as determined from the temperature dependence of the ratio of thermionic emission to electrical conduc-

tivity, were essentially independent of the states of activation. Changes in the surface dipole of BaO were observed by Dueker and Hensley⁵ by evaporating barium onto a cold cathode, but these changes were permanently removed by subsequent heating of the cathode.

In kinetic-energy distributions, electrons excited directly from donor levels appear as "fast peaks," that is, peaks which increase their kinetic energy by amounts equal to the increase in photon energy. The kinetic-energy distributions in Fig. 3, which were obtained from a cathode in a high state of activation, show a well-pronounced fast peak for the lower photon energies. However, for photon energies above about 4.1 eV, this peak becomes distorted. The right shoulder of the peak continues to move to the right with increasing photon energy but its amplitude apparently decreases and a slower distribution of electrons appears on the low-energy side. This suggests that electrons are being inelastically scattered from the fast peak, resulting in a straggling of electrons to lower kinetic energies.

For each of the curves in Fig. 3, the difference between the kinetic energy of the fast peak and the photon energy is shown below the peak. Since for photon energies above 4.1 eV the peak is obscured by the straggling of electrons, the position of a 2.9-eV peak is indicated showing these distributions to be consistent. From these and similar distributions, a donor about 2.9 eV below the vacuum level is inferred. Note that for the photon energy of 2.8 eV, the peak of the distribution would fall below the vacuum level so that the fast peak seen in the lowest curve in Fig. 3 has been truncated by the surface barrier.

Kinetic-energy distributions for a cathode of intermediate activation are shown in Fig. 4. Again the fast peak is observed to become distorted at photon energies above 4.1 eV. Since the shoulders at the right edges of these distributions are somewhat better defined for this tube, the actual position of the fast peak has been estimated for each curve. For this tube, the data indicate a second donor about 3.7 eV below the vacuum level. Other cathodes gave slightly lower values, so that it is estimated that this donor lies about 3.6 ± 0.1 eV below the vacuum level. In this investigation, only one tube had just the right degree of activation, so that fast peaks from both the 2.9- and 3.6-eV level appeared simultaneously.

As was mentioned above, a possible explanation for the distortion of the fast peaks in the kinetic-energy distributions involves a straggling of electrons from the fast peaks; that is, some of the electrons in the fast peaks lose energy through scattering processes as they approach the surface of the solid. Evidence for this may be seen in the fact that the fast peaks continue to grow in amplitude as the photon energy is increased until the onset of distortion. Beyond this point, the amplitude of the fast peak, now represented by a

⁶ G. A. Saum and E. B. Hensley, *Phys. Rev.* **113**, 1019 (1959).

⁷ R. J. Zollweg, *Phys. Rev.* **111**, 113 (1958).

shoulder, begins to decrease although the total area under the curve continues to increase.

An important clue to the mechanism involved in the distortion of the fast peaks is found in the fact that the onset of the straggling depends on the photon energy and not on the kinetic energy of the electrons. In Fig. 4, in which the fast peak from the 3.6-eV donor dominates, the onset of the straggling occurs when the fast peak reaches a kinetic energy of about 0.4 eV. In Fig. 3, in which the fast peak from the 2.9-eV donor dominates, the onset of the straggling does not occur until the kinetic energy of the peak reaches about 1.2 eV. However, the onset of the straggling occurs in each of the above cases when the photon energy has increased to about 4.1 eV.

The above observation suggests that the mechanism for the straggling process involves the excitation of large densities of electrons from the valence band to the conduction band. The threshold for such transitions should occur at about 3.4 eV, the width of the band gap. However, the probability of such transitions would not become large until substantially larger photon energies were reached. Presumably at about 4.1 eV, the probability for these band-to-band transitions has reached a sufficiently large value for the density of electrons in the conduction band to cause inelastic scattering of the electrons in the fast peaks. Whether this process is simply a matter of electron-electron scattering or another mechanism which depends on a high density of conduction-band electrons cannot be stated at the present time.

It is tempting to speculate that the defects responsible for the 3.6- and 2.9-eV centers are the F and F' centers in BaTe, that is, tellurium ion vacancies containing one electron and two electrons, respectively. Such optical-absorption centers have not yet been observed in BaTe but have been identified in the alkaline-earth oxides.⁸ It is probable that these centers are also the donors responsible for the activation of the thermionic emission from BaTe reported by Brown and Hensley.² This study indicated two donors at thermal transition energies 2.2 and 3.2 eV below the vacuum level.

Unlike the photoelectric emission from BaO,^{4,5} no two-step process involving excitons was observed for BaTe. Such a process would have manifested itself by the appearance in the kinetic-energy distributions of a "slow" peak, that is, a peak whose kinetic energy remained constant for increasing photon energies above the threshold for exciton absorption. Also, no prominent peaks in the total yield corresponding with the peaks in the exciton absorption spectra at 3.10, 3.65, and 4.08 eV were observed.^{6,7}

⁸ J. C. Kemp, W. M. Ziniker, and E. B. Hensley, *Phys. Letters* **25A**, 43 (1967); W. C. Ward and E. B. Hensley, *Bull. Am. Phys. Soc.* **10**, 307 (1965); B. P. Johnson and E. B. Hensley, *ibid.* **11**, 411 (1967).

This absence of an exciton-induced component in the photoelectric emission from BaTe is easily understood. It has been shown that in BaO the excitons degrade in energy, presumably due to some form of relaxation, before they can give up their energy to a donor electron.⁵ Because the first exciton absorption in BaTe has an energy of 3.1 eV, any substantial degradation of this energy would leave insufficient energy for an electron from either the 2.9- or 3.6-eV states to escape from the solid.

Also, unlike the total photoelectric yield from BaO,^{5,9} no shoulders were observed in the photoelectric-yield spectra of BaTe which correspond with the two bound states. This can be understood by observing in Figs. 3 and 4 that the quantum efficiencies for the transitions from these centers increase rapidly with increasing photon energy. This is in contrast to the behavior in BaO, where it was observed that the fast peaks remained at the same level as they moved to higher kinetic energies with increasing photon energies.⁵

A behavior similar to that for BaTe has also been observed in the total photoelectric yield for SrO.¹⁰ Here again, the quantum efficiency of the fast peaks was observed to increase with the photon energy and no structure associated with the donors could be identified in the total yield spectra.

V. CONCLUSIONS

From the threshold for the photoelectric emission from the valence band, the energy of the top of the valence band in BaTe was estimated to be 4.8 eV below the vacuum level. Using an estimate of the band gap of 3.4 eV, the electron affinity of BaTe was estimated to be 1.4 eV. Direct photoelectric emission from two bound states lying 2.9 and 3.6 eV below the vacuum level was observed. The quantum efficiencies for these transitions were observed to increase with increasing photon energy. Consistent with this change in quantum efficiency, no structure corresponding to the bound-state energies was observed in the total photoelectric yield. At photon energies above about 4.1 eV, the fast peaks in the kinetic-energy distributions were observed to become distorted. This was attributed to the inelastic scattering of electrons as a result of large densities of electrons being excited to the conduction band for photon energies above 4.1 eV. Unlike the photoelectric emission from BaO, no evidence for an exciton-induced component in the emission was observed. This was shown to be consistent with the proposed model for BaTe.

⁹ E. Taft, H. Philipp, and L. Apker, *Phys. Rev.* **113**, 156 (1959).

¹⁰ H. D. Rutledge, Ph.D. thesis, University of Missouri, Columbia, Missouri, 1966 (unpublished).