

## Photoelectric Emission from Barium Oxide\*

JAMES E. DUEKER† AND EUGENE B. HENSLEY

*Department of Physics, University of Missouri, Columbia, Missouri*

(Received 4 May 1964)

The photoelectric emission from barium oxide has been investigated by measuring the total photoelectric yield and the distributions in kinetic energy of the emitted electrons using an improved magnetic velocity-analyzer tube. The energy distribution measurements revealed four "fast peaks" which are interpreted as being associated with direct transitions from energy levels located approximately 1.0, 1.4, 2.0, and 2.6 eV below the vacuum level. Confirmation of these transitions was obtained from plots of the spectral distribution of the total photoelectric yield. A "slow peak" was observed in the energy distributions at about 0.5 eV which is attributed to exciton-induced photoelectric emission. Evidence is presented indicating that this is a true peak and not the truncated tail of a distribution which peaks at still lower energies. Possible identifications of the energy levels involved in the direct transitions and the energy loss mechanism involved in the exciton-induced transitions are discussed.

### I. INTRODUCTION

THE photoelectric emission from barium oxide has previously been studied using measurements of the spectral distribution of the total photoelectric yield<sup>1-4</sup> and the kinetic energy distribution of the emitted electrons.<sup>2,3</sup> Philipp<sup>3</sup> employed a magnetic velocity analyzer to obtain the kinetic energy distribution. Preliminary to extending his method to a study of other materials, an innovation in the technique unexpectedly resulted in substantially improved resolution of details in the distributions. The present investigation represents an extension of the previous studies of the photoelectric emission from barium oxide utilizing this improved resolution.

### II. EXPERIMENTAL PROCEDURES

In the magnetic velocity-analyzer method, electrons emitted from a cathode by monochromatic light are first accelerated through a fixed potential and are then bent in a semicircular path by a magnetic field produced by a pair of Helmholtz coils. A set of three slits in an analyzer box defining a semicircular path, select electrons having a particular energy in a manner similar to a miniature  $\beta$ -ray spectrometer. As employed by Philipp, the accelerating potential was held fixed and the magnetic field was varied in order to scan the kinetic energy distribution of the emitted electrons. In the present investigation, the magnetic field was held fixed, and the initial accelerating potential was varied. While this procedure has the advantage that the observed kinetic energy will vary linearly with the applied accelerating potential it has the undesirable feature of changing the electric field at the cathode. To avoid this defect, an auxiliary slit was placed between the analyzer chamber and the cathode. An un-

expected result from this arrangement was that by maintaining the field at the cathode near zero, greatly improved resolution of the structure of the kinetic energy distribution was obtained. This loss in resolution due to a strong electric field at the cathode is attributed to a nonuniform potential at the surface of the cathode resulting from nonuniform *IR* drops in the coating. This nonuniform potential would cause electrons from different portions of the cathode to receive differing amounts of acceleration with a consequent smearing of details in the distribution.

It was also found that the resolution could be still further improved by keeping the light intensity on the cathode as low as possible, consistent with maintaining sufficient photocurrent for reliable measurements. The loss in resolution due to high light intensity is probably complex, involving such factors as depletion of electrons from the donors, internal space charges, and nonuniform *IR* drops, all contributing to a nonuniform surface potential.

Except for the addition of the auxiliary slit between the analyzer chamber and the cathode and the structure of the cathodes themselves, the tubes employed in this investigation were similar to those used by Philipp.<sup>3</sup> The three slits in the analyzer chamber defined a semicircular path for the electrons 3 cm in diameter. The entrance and exit slits were 0.1 mm wide, the intermediate slit was 0.5 mm wide. The auxiliary slit was made slightly wider than the entrance slit to facilitate alignment.

Three different cathode structures were used in this investigation. The first of these was a planar cathode of commercial design similar to that employed by Philipp. The other two cathodes were both designed to provide cooling to liquid-air temperature. The first of these consisted of a 0.25-in. platinum tube mounted as an extension on the bottom of a liquid-air Dewar and passed parallel to the entrance slit of the analyzer. The oxide coating, deposited on the surface of this tube opposite the slit, could be heated by inserting a heater into the tube, or cooled by filling the tube with liquid air. In the alternate design, the oxide coating was

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

† Present address: McDonnell Aircraft Corporation, St. Louis, Missouri.

<sup>1</sup> H. B. DeVore and J. W. Dewdney, *Phys. Rev.* **83**, 805 (1951).

<sup>2</sup> L. Apker, E. Taft, and J. Dickey, *Phys. Rev.* **84**, 508 (1951).

<sup>3</sup> H. R. Philipp, *Phys. Rev.* **107**, 687 (1957).

<sup>4</sup> E. Taft, H. Philipp, and L. Apker, *Phys. Rev.* **113**, 156 (1959).

deposited on a nickel ribbon supported between two tungsten rods projecting from the bottom of the Dewar. It was found that the cathodes could be adequately cooled by the thermal conduction through these tungsten rods. In this latter design, the cathodes were heated by passing current through the ribbon.

Most of the tubes used in this investigation employed cathodes formed by vapor deposition. In these tubes the analyzer chamber was arranged so that it could be moved along tungsten guide rods, parallel to the cathode. On the lower side of the analyzer chamber were mounted the barium or barium oxide evaporators.

Barium oxide coatings used in this investigation were prepared in three different ways: thermal reduction of sprayed coatings of BaCO<sub>3</sub>, oxidation of evaporated films of barium, and directly evaporated films of barium oxide.

The sprayed cathodes were prepared from a spray suspension of BaCO<sub>3</sub> in Raytheon binder B71-5 following the usual procedures.<sup>5</sup> The areal density of the coatings were about 10–15 mg/cm<sup>2</sup>. The tube was baked at 450°C both before and after thermal conversion of the carbonate to the oxide. The maximum temperature of the cathode after conversion was 1325°K. Getters were flashed in a side arm and the tube was sealed off with the pressure about 10<sup>-8</sup> Torr. The cathodes were activated by drawing space-charge limited current with the cathodes at 1125°K.

The second method for preparing the barium oxide cathodes was to oxidize evaporated films of barium metal. The barium evaporators consisted of Kemet KIC barium getters. The oxygen was admitted to the tube by diffusion through a silver side arm heated to 800°C. After the barium film had been oxidized, the excess oxygen was removed by flashing a getter in a side arm. These cathodes were then activated as before by drawing space-charge limited emission.

The third method of preparation was the direct evaporation of barium oxide onto the cathode substrate. The evaporators consisted of coils of platinum wire on which barium carbonate spray suspension had been painted. After the carbonate had been converted to the oxide by thermal decomposition, the tube was sealed off from the vacuum system. Barium oxide was then evaporated onto the cathode substrate making use of empirical data obtained by Russell and Eisenstein.<sup>6</sup> They found that barium oxide evaporated at the rate of one monolayer per half-hour with the evaporator at 1310°K and at a distance of 7 mm. The cathodes were then activated as before by drawing space-charge limited current.

For measurement, the tubes were mounted in a light tight box located in the center of a pair of Helmholtz coils. Two light sources were used, a 750-W tungsten

filament projection lamp for photon energies from 0.75–3.0 eV and a General Electric type AH-6 mercury arc for photon energies from 3.0–5.0 eV. A Gaertner quartz prism monochromator was used with a slit width of 0.1 mm resulting in a band pass of about 0.04 eV at 4 eV. Absolute light intensities were measured using type 935 and type 915 photocells which had previously been calibrated using a standardized Gaertner thermopile. The collector current was measured with an Applied Physics Model 210 vibrating reed electrometer, the output of which was fed to an L & N Speedomax recorder.

The current in the Helmholtz coils was held constant to better than 0.1% and at such a value that the kinetic energy of the electrons traversing the slits in the analyzer was about 6 eV. The exact calibration to establish the zero for the kinetic energy scale was obtained by making measurements of the distributions for thermionic emission as described by Philipp.<sup>8</sup> An automatic cycling device was used to minimize enhancement effects. A light shutter was opened for 10 sec during which time the collector current was recorded. The light shutter was then closed for 30 sec and the anode voltage was advanced 0.05 V. At frequent intervals the light intensity was checked manually during the light-off periods.

Total photoelectric yield measurements were made with the auxiliary slit and analyzer chamber connected together. Particular care was taken to make these measurements at low light levels to avoid depletion of electrons from the donors.

### III. RESULTS

Of the three methods used for the preparation of cathodes, the direct evaporation of barium oxide was found to give the most satisfactory results. Most of the measurements were made at liquid-air temperatures. The curves with closed points in Fig. 1 represent the kinetic energy distributions from a typical cathode for four different photon energies. In the upper three of these curves a slow peak is observed at about 0.5 eV, which increases in magnitude but does not shift position with increasing photon energy. This is similar to the slow peak observed by Philipp<sup>8</sup> and is attributed to exciton induced photoelectric emission. Four fast peaks which shift to higher kinetic energies as the photon energy is increased are observed. Subtracting the kinetic energies for these peaks from the corresponding photon energies leads to the binding energies (depths below the vacuum level) of the donor electrons giving rise to these peaks. These energies are marked at the tops of the stepped lines indicating the positions of these peaks. The observed peaks are rather irregular and poorly defined. However, they were consistently observed to occur within about 0.1 eV of the indicated values of 1.0, 1.4, 2.0, and 2.6 eV in each of 42 curves obtained from six different cathodes in a total of 18 different states of activation.

<sup>5</sup> *Tube Laboratory Manual* (Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, 1956), 2nd ed.

<sup>6</sup> P. N. Russell and A. S. Eisenstein, *J. Appl. Phys.* **25**, 954 (1954).

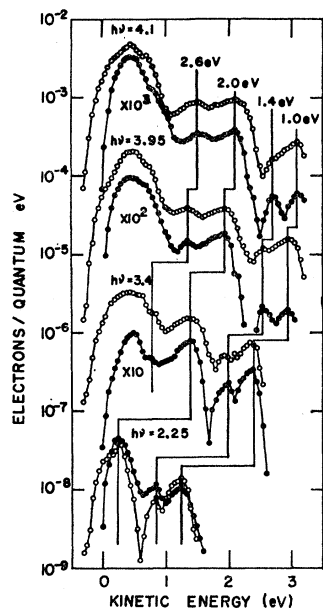


FIG. 1. Energy distribution of the photoelectric emission from two cathodes for four different incident photon energies. The closed points are data from a barium oxide cathode formed by vapor deposition. It was activated by drawing space charge limited emission at a temperature of 1125°K. The open points are data from the same cathode after approximately 0.6 monolayers of barium had been deposited at room temperature. All measurements were made with the cathodes at liquid-air temperature.

As will be discussed later, a question has been raised as to whether the slow peak above is a true peak or whether it is the truncated shoulder of a distribution which has its true maximum below the vacuum level of the cathode. To aid in distinguishing between these two possibilities, an experiment was devised to attempt to lower the electron affinity of the cathode by depositing a partial monolayer of barium on its surface. After the data represented by the closed points in Fig. 1 were obtained, barium was deposited on the surface of the cathode at room temperature to a calculated thickness of 0.6 monolayer. The energy distribution measurements were then repeated and are shown in Fig. 1 as the open points. The calibration for the kinetic energy scale was left unchanged from the previous runs. A small increase in the photoelectric yield is observed. No significant change in sharpness or positions of either the fast or slow peaks is observed. However, the low-energy tail of the slow peak is seen

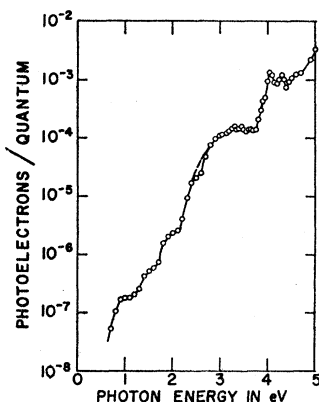


FIG. 2. Spectral distribution of the total photoelectric yield from the same cathode represented by the closed points in Fig. 1. Measurements were made with cathode at liquid-air temperature.

to extend several tenths of an electron volt into the negative kinetic energy region as would be expected if the electron affinity was lowered by the partial monolayer of barium. These observations indicate that the slow peak is a true peak and is not the truncated tail of a lower lying peak.

In Fig. 2 is shown a plot of the total yield from the same cathode as that from which the data represented by the closed points in Fig. 1 was taken. Shoulders<sup>7</sup> may be seen which are consistent with the donor energies indicated by the four fast peaks in the kinetic energy distributions.<sup>8</sup> At higher energies, peaks can be seen at 3.9, 4.0, and 4.3 eV which correspond with the exciton peaks observed in the absorption spectrum of barium oxide.<sup>9</sup>

The photoelectric emission from several cathodes of BaO formed by thermal reduction of BaCO<sub>3</sub> was measured. However, the structure of the total yield plots and the kinetic energy distribution plots were more irregular and much less reproducible than were the measurements obtained from cathodes prepared by the other two methods. These difficulties are attributed to the difficulties in obtaining cathodes of this type with uniform activation and consequently a uniform surface potential.

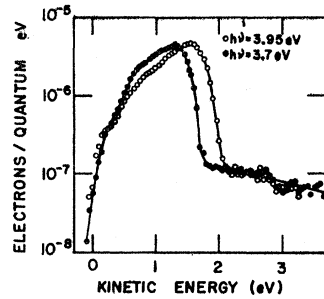
In the tubes in which the cathodes were prepared by oxidizing thin films of barium metal, some measurements were made on the unoxidized metal films. A Fowler plot of the total yield from these films gave a good fit to the theoretical curve over three orders of magnitude. The photoelectric work function for barium determined from this plot was 2.38 eV in close agreement with the value of 2.3 eV obtained by Apker, Taft, and Dickey.<sup>2</sup> Plots of the kinetic energy distributions of the photoelectrons for two different photon energies are shown in Fig. 3. Because of the high vapor pressure of barium, it was not practical to use ther-

<sup>7</sup> Shoulders in the total photoelectric yield are expected in barium oxide since the amplitudes of the fast peaks in the energy distributions are observed to remain constant with increasing photon energy. From this it may be concluded that the transition probabilities for electrons in the donor states to states in the continuum above the vacuum level are essentially independent of the photon energy. As a consequence, the total photoelectric yield would have a tendency to level off as the photon energy increases beyond the median energy for each donor, and would only begin to increase again as a result of transitions from the next deeper donor. It should be emphasized that this is not necessarily typical behavior. For example, the amplitudes of the fast peaks in the kinetic energy distributions for barium telluride have been observed to increase markedly with increasing photon energies. Consistent with this behavior, no indication of shoulders corresponding to donor energies were observed in plots of the total photoelectric yield. [F. E. Martin and E. B. Hensley, *Bull. Am. Phys. Soc.* **9**, 428 (1964).]

<sup>8</sup> Figure 2 is not completely typical of the total yield plots in that they usually did not have the break at 2.6 eV but continued smoothly as indicated by the dashed line. This figure was chosen simply because it represents data from the same cathode from which the data in Fig. 1 was taken. In general, the total yield plots were not found to be as reliable for detecting the presence of donors and determining their energies as were the energy distributions.

<sup>9</sup> R. J. Zollweg, *Phys. Rev.* **97**, 288 (1955).

FIG. 3. Energy distribution of the photoelectric emission from a metallic barium cathode for two incident photon energies. Measurements were made with cathode at room temperature.



mionic emission measurements to establish the zero for the kinetic energy scale for the plots. Consequently the zero was assigned to agree with the threshold of the distributions.

The sharp drop on the high-energy side of the distributions in Fig. 3 represents the distribution of electrons within the metal near the Fermi energy. The kinetic energy of the electrons ejected from the Fermi level should correspond to the points where the distributions drop to one-half their peak values. If these energy values are subtracted from the corresponding photon energies, an apparent photoelectric work function of about 2.16 eV is obtained. The discrepancy between this value and the value of 2.38 eV obtained from the Fowler plot can be understood if the lowest energy electrons originate from patches (perhaps of barium oxide) having a work function about 0.2 eV lower than for the rest of the surface. The shape of the distribution curves in this low-energy region is consistent with such an explanation.

At room temperature the Fermi factor changes from 0.9 to 0.5 in an energy change of 0.057 eV. In Fig. 3, the corresponding change takes place in an energy change of 0.125 eV. This gives a direct indication of the resolution of the apparatus.

The barium films were oxidized by admitting oxygen through a silver side arm and were then activated by drawing space-charge limited thermionic emission. In Fig. 4 are shown plots of the kinetic energy distributions obtained from such a cathode. Two fast peaks at 1.0 and 1.4 eV and a slow peak at a kinetic energy of about 0.5 eV are seen at amplitudes comparable to those previously observed. However, a very

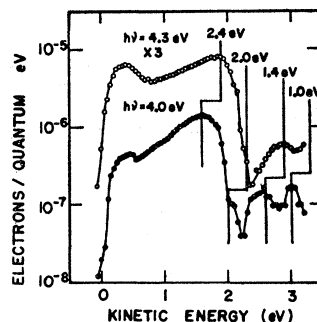


FIG. 4. Energy distribution of the photoelectric emission from a cathode prepared by oxidizing a film of barium metal. Measurements were made with cathode at liquid-air temperature.

strong fast peak is observed at about 2.4 eV which is much stronger in amplitude than any of those previously observed. Comparison of this fast peak with the kinetic energy distribution obtained from thin films of barium metal seems to indicate that this peak is probably due to unoxidized barium still present in the film, possibly in the form of colloidal particles. Although barium oxide cathodes were easily prepared with this technique, the difficulty of eliminating the effects of residual amounts of metallic barium made this method of preparation unsuitable for the present study.

#### IV. DISCUSSION

Four fast peaks were consistently observed in the kinetic energy distributions. These indicate the existence of four distinct donor levels in barium oxide at low temperatures. Confirmation of the presence of these levels was obtained from the total photoelectric yield data. This latter is particularly significant since the total yield should be essentially unaffected by nonuniformities in the work function and thus rules this out as a possible explanation of the large number of fast peaks observed.

At the present time it does not appear to be possible to make positive identifications of the four levels giving rise to the transitions observed in this investigation. However, one of the most attractive possibilities is that the principal donors in barium oxide are associated with electrons in oxygen vacancies.

Sproull, Bever, and Libowitz<sup>10</sup> have correlated the blue optical absorption having a peak at 2 eV in single crystals of barium oxide with oxygen vacancies. Carson, Holcomb, and Buchardt<sup>11</sup> attempted to observe a paramagnetic resonance associated with these blue color centers and from their negative result concluded that these vacancies contain two electrons. That is, they are  $F^2$  centers.<sup>12</sup> Thus, a possible identification of two of the donors observed would be  $F^1$  and  $F^2$  centers. An  $F^3$  center, analogous to the negatively charged  $F'$  center in the alkali halides is unlikely since it would not exist under conditions of thermal equilibrium. The other two centers could possibly be complexes of the  $F^1$  and  $F^2$  centers formed at low temperatures. However, it must be emphasized that these identifications are merely conjectures and have not been established.

The slow peak observed in the kinetic energy distributions has been ascribed by Philipp<sup>8</sup> to a two-step process in which the photon is first adsorbed in the formation of an exciton, which in turn gives up its energy to a donor electron. This type of process was

<sup>10</sup> R. L. Sproull, R. S. Bever and G. Libowitz, Phys. Rev. **92**, 77 (1953).

<sup>11</sup> J. W. Carson, D. F. Holcomb, H. Buchardt, Phys. Chem. Solids **12**, 66 (1959).

<sup>12</sup> Analogous to the  $F'$  centers in the alkali halides, the notation  $F^s$  has been suggested [E. B. Hensley, J. Appl. Phys. **32**, 301 (1961)] where  $s$  indicates the number of electrons in the anion vacancy.

first observed by Apker and Taft<sup>13</sup> in the photoelectric emission from RbI.

In the above process the kinetic energy of the slow peak electrons is observed to be much less than the difference between any combination of an exciton adsorption peak and a donor binding energy as determined by the fast peaks. Consequently, an additional loss in energy must occur at some stage in the process. Two separate theories were considered by Apker and Taft to account for this loss in energy. The first, which was suggested by Hebb, postulates that a dead layer exists at the surface of the material such that the electrons ejected by the excitons must traverse a minimum region before escaping from the surface. The slow peak is interpreted as being the truncated tail of a distribution of electrons degraded by inelastic scattering and peaking at a still lower value of kinetic energy. In the second theory, first suggested by Seitz, the loss in energy takes place by a degradation of exciton energy before donor electron stimulation. Although peaks in the exciton absorption are observed at four different energies, the final energy of the exciton is probably peaked at a single value.

In order to distinguish between the above two theories, the experiment was carried out in which partial monolayer of barium metal was deposited on the surface of the barium oxide. It was anticipated that this would result in a lowering of the surface potential barrier. Thus, if the slow peak were the truncated tail of a distribution of electrons peaking at still lower energies, the slow peak would be expected to move to lower energy. As can be seen in Fig. 1, the experiment was apparently successful in being able to lower the surface potential barrier as the low energy tail of the kinetic energy distribution was extended approximately 0.3 eV. However, the position of the slow peak was unaltered relative to the original distribution and also relative to the positions of the fast peaks. From this it is concluded that the degradation of the exciton energies is the more plausible explanation of the energy loss observed in barium oxide.<sup>14</sup>

The question now arises as to the value of the energy to which the exciton degrades in the above process. This could be determined if the donor from which the electrons are ejected to form the main slow peak at 0.5

eV could be identified. Of the four donor levels indicated by the four fast peaks, all but the 1.0-eV peak would result in additional structure in the slow peak. For example, if the degraded exciton energy were 1.9 eV, electrons from the 1.4-eV donor level would produce a slow peak with a kinetic energy of 0.5 eV and electrons from the 1.0-eV donor level would produce a second peak with a kinetic energy of about 0.9 eV. Some such structure is usually observed in the slow peak as can be seen in Fig. 1. However, quantitatively the magnitude of this structure is not as pronounced as would be expected from the relative magnitudes of the 1.0 and 1.4 fast peaks. A degraded exciton energy of 2.5 eV would result in a strong slow peak at 0.5 eV due to electrons from the 2.0-eV donor level and lesser peaks at kinetic energies of 1.1 and 1.5 eV. Since the magnitudes of the 1.4- and 1.0-eV fast peaks indicate lower densities for these levels, the details of the resulting slow peak structure would probably be obscured by the fast peaks. Finally, the possibility in which the degraded exciton energy is 3.1 eV is unlikely as this would predict two slow peaks of approximately equal magnitude at 0.5- and 1.1-eV kinetic energy.

Thus, a unique determination of the degraded exciton energy does not appear possible from the results of the present investigation. However, from these results a value of either 2.5 or 1.9 eV appear to be the most probable. Experiments in which the relative densities of the donors is varied, perhaps by deactivating the cathodes or in which higher photon energies are used in order to more completely display the high-energy side of the slow peak, could possibly resolve this uncertainty. However, such attempts in the present investigation proved to be beyond the sensitivity of the apparatus.

One further piece of evidence may have a bearing on the above question. Stout<sup>15</sup> has observed the luminescence from barium oxide as a function of activation and temperature. Any luminescence resulting from the degraded exciton would be expected to increase in intensity with both decreasing activation and temperature. One peak in the luminescence spectra was observed to have these characteristics. Its energy of 2.7 eV is not in good agreement with the 2.5 eV possibility above but perhaps this is due to experimental inaccuracies.

#### ACKNOWLEDGMENT

The authors are grateful to Professor Bernard Goodman for helpful discussions concerning this investigation.

<sup>15</sup> V. L. Stout, Phys. Rev. **89**, 310 (1953).

<sup>13</sup> L. Apker and E. Taft, Phys. Rev. **82**, 814 (1951).

<sup>14</sup> This conclusion does not necessarily apply to RbI (see Ref. 13). In this connection it should be noted that the slow peak for RbI occurs at a kinetic energy of about 0.3 eV, or about 0.2 eV lower than for BaO and is much more asymmetric. These observations lend additional support to the slow peak in BaO being a true peak.