shown in Figs. 1(b) and (c) with air rather than BaO between the electrodes.[12] In electrostatic units

$$C=(r^2/4t)+(r/2\pi)(1-\ln 2);\quad (t/r)\ll 1,$$

where r is the electrode radius and t is the thickness of the air-gap. The first term is the familiar major term, the second is an end correction term from the charge collected on the flat surface near the intersection of the cylindrical and flat circular surfaces. The end correction from charge on the cylindrical surfaces cannot be correctly obtained by conformal mapping (since this method strictly applies to two-dimensional problems only), and it is omitted here for the following reason: if one introduces a slab of BaO instead of air, its periphery being shaped like the outermost line of force from charge on the intersection between the cylindrical and flat circular surfaces, then the field in the surrounding air remains undistorted. Hence, the difference between the BaO and air condenser capacitance is

$$\Delta C=(\kappa-1)[(r^2/4t)+(r/2\pi)(1-\ln 2)], \tag{1}$$

where κ is the dielectric constant of BaO. By using only the major term,

$$\Delta C=(\kappa-1)(r^2/4t), \tag{2}$$

the calculated κ for a 0.051-cm thick slab of BaO, 0.478 cm in diameter, is 4 percent too high; for a 0.0255-cm thick slab it is 2 percent too high.

Since the shape of the actual periphery of the slab of BaO was far from the ideal, the edge effect was also investigated experimentally. A series of measurements on polycrystalline sample No. 5P of diameter 0.0470 cm gave the results shown in Table II. Electrode contact as in Fig. 1(c) had to be used for thin samples. For these, sufficient pressure to obtain good electrical contact could not be applied with the aluminum foil without shorting the electrodes. The data indicate that random errors in measurement make end effect corrections quite insignificant.

---

[12] This problem is similar to finding the magnetic field between the magnetic poles of a cyclotron, as discussed by M. E. Rose, Phys. Rev. 53, 715 (1938).

PHYSICAL REVIEW VOLUME 83, NUMBER 4 AUGUST 15, 1951

Photoconductivity and Photoelectric Emission of Barium Oxide

HENRY B. DEVORE AND JOHN W. DEWDNEY*
RCA Laboratories Division, Radio Corporation of America, Princeton, New Jersey

(Received December 26, 1950)

Barium oxide, in the form of a sprayed coating on a nickel base, was investigated by means of studies of photoconductivity, photoemission, and absorption measurements and the variation of these with temperature. Changes occurring during activation of the oxide were observed. The results are discussed in terms of an energy level structure for barium oxide.

I. INTRODUCTION

THE literature on the oxide cathode is replete with investigations undertaken to establish constants on which to set up a picture of the electron energy band structure for the (Ba, Sr)O emissive coating.[1] Very few of these studies have been concerned with the individual components of these coatings. One of the earliest of these is reported by Nishibori *et al.*,[2] wherein studies of the conductivity and thermionic and photoelectric emissions were combined to derive values for the electron affinity and Fermi level for BaO and SrO, as well as for the combined form.

More recently, Tyler,[3] working with barium oxide single crystals prepared by Sproull, as well as with evaporated films, has studied the optical absorption and photoconductivity. The location of the absorption edge (~3.8 ev) reported by Tyler has been confirmed by Taft and Dickey[4] on the basis of studies of photoelectric emission from thin metallic layers deposited on a base of barium oxide. Apker, Taft, and Dickey[5] have reported studies of the photoelectric emission from BaO which indicate an energy for the top of the filled band 5.0–5.2 ev below vacuum potential.

In the work reported here, photoconductivity, photoelectric emission, and optical reflectivity measurements have been made on barium oxide, as formed, and have been followed through the activation process in order to obtain further information concerning the energy level structure.

II. EXPERIMENTAL

Figure 1 shows the form of the tubes used in this work. Barium carbonate (Mallinckrodt Ultra Pure), dispersed in a nitrocellulose binder, was sprayed on a cathode sleeve of N-81 (pure) nickel to give a coating weight of 10–15 mg/cm². A probe wire of pure platinum, 0.001 in. diameter, was wound over this coating, and a second thin coating of the carbonate was sprayed over the probe wire, primarily to seal it in place. The anode cylinder, also of N-81 nickel, was provided with longitudinal slots to permit irradiation and observation of the oxide surface. The electrode assembly was sealed into an envelope having a fused quartz section sur-

---

* Now at Sir George Williams College, Montreal, Quebec.

[1] A. S. Eisenstein, Advances in Electronics 1, 1–64 (1948); J. P. Blewett, J. Appl. Phys. 10, 668 (1939); 10, 831 (1939); 17, 643 (1946).

[2] E. Nishibori and H. Kawamura, Proc. Phys.-Math. Soc. Japan 22, 378 (1940); Nishibori, Kawamura, and Hirano, Proc. Phys.-Math. Soc. Japan 23, 37 (1941).

[3] W. W. Tyler, Phys. Rev. 76, 179(A) (1949); 76, 1887 (1949); dissertation, Cornell University, Ithaca, New York (1949).

[4] E. A. Taft and J. E. Dickey, Phys. Rev. 78, 625 (1950).

[5] Apker, Taft, and Dickey, Phys. Rev. 76, 453(T) (1949).

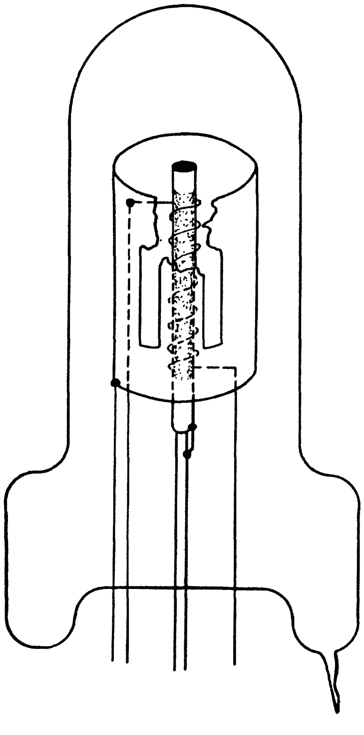

FIG. 1. Experimental tube.

rounding the anode. After exhaust and bakeout, the cathode was converted from carbonate to oxide by heating slowly to approximately 1200°K, the heating being continued until gas evolution has substantially ceased. A small part of the available getter was then flashed, and the tube sealed off.

Temperatures of the oxide coating, in the range in which most of the work was done (300°K–700°K), were measured by using the platinum probe wire as a resistance thermometer.

The arrangement of apparatus used is indicated in Fig. 2. A Perkin-Elmer model 12 infrared spectrometer, with a crystal quartz prism, is used as a monochromator to illuminate the oxide. The light from a high pressure mercury arc, G.E. Type A-H6, is focused on the entrance slit through a sector disk which chops the light at a 23.5-cycles/second rate to give intermittent illumination. This permits separation of photocurrents from any dark current present. After passing through the monochromator, half the light is reflected from the exit beam and focused on a thermistor bolometer (Western Electric Type V-649) for energy measurement. The remainder of the beam is focused on the oxide cathode in an adjoining shielded and lighttight box. A neutral wedge W, placed just ahead of the entrance slit, has its position servo-controlled from the thermistor output so as to maintain the output of the monochromator nearly constant in power, with 1.5×10^{-6} watt falling on the oxide surface, for all spectral regions. With the H6 lamp source, the system operates satisfactorily over the range from 8200A (1.5 ev) to 2750A (4.5 ev). The lamp output is insufficient to permit measurements at higher photon energies.

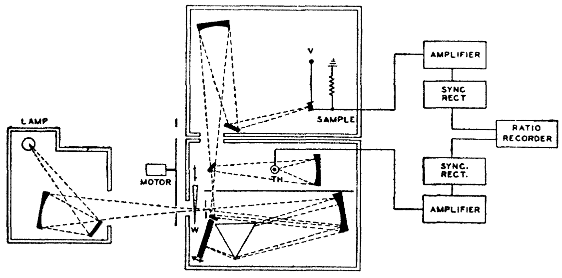

FIG. 2. Arrangement of apparatus.

For photoelectric emission studies, the cathode and probe are held at a negative potential considerably greater than required for saturation, and the anode is connected through a standard resistor to ground. The photocurrent signal developed across this resistor is taken to an amplifier tuned to the 23.5-cycles/second chopping frequency. The amplified signal is converted to dc by a phase sensitive rectifier, synchronized with the light chopper, and this is followed by a low pass filter with a cut-off characteristic which can be adjusted to set the over-all band width to values between 1 and 0.1 cycle-second. The thermistor signal is passed through a similar system, and the two signals are fed to a Brown recording potentiometer which has been modified to operate as a ratio recorder. As the spectrum is scanned by the monochromator, the recorder draws a curve showing photocurrent per unit energy through the spectrum.

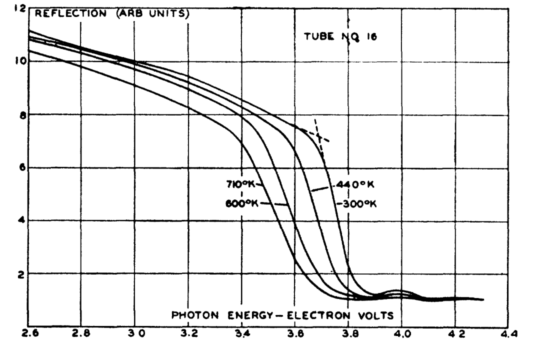

FIG. 3. Reflection from unactivated BaO.

For photoconduction measurements, in order to reduce polarization phenomena, an alternating voltage at 60 cycles/second is applied to the nickel cathode base and the probe connected through the standard resistor to ground. With the 23.5-cycle/second illumination, this yields photoconduction current signals at the beat frequencies. The current is measured with amplifier and rectifier tuned to 36.5 cycles/second.

In measurements made in this manner, the possibility always exists that photoemission measurements may be affected by the photoconductive effect, since the body of the oxide is effectively in series with the emitting surface. Conversely, the photoconductivity measurements may be confused by photoelectric emission from the surface above the probe wire to surrounding electrodes and to the rest of the cathode surface, and vice versa. While it is not possible to assert that these effects have been completely eliminated, they are believed to be of negligible importance in these experiments. This is based on the observations that: (1) photoemission currents were always measured under saturation conditions; (2) in one case in which a tube became gassy, so that photoemission could no longer be observed, the photoconduction curve was found to be substantially identical with that observed under high vacuum conditions; and (3) the photoemission and photoconduction curves were, in fact, found to be different in character and to show different behaviors with temperature and with activation.

With the barium oxide in the form of a cathode coating, direct optical absorption measurements are not feasible. However, useful information as to the location of the absorption edge may be inferred from measurements of reflectivity. For this purpose, a photomultiplier tube (1P28) is set up to view the cathode surface through an anode slot adjacent to that through which the incident radiation passes. A spectral curve is taken in this way and another made with the radiation falling directly on the multiplier surface. The curves are divided, point by point, to obtain a reflectivity curve.

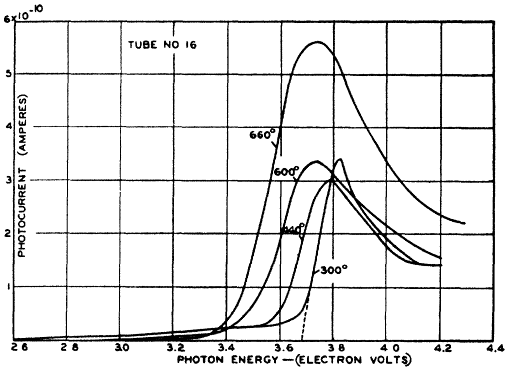

FIG. 4. Photoconductivity in unactivated BaO.

The barium oxide, after the exhaust and breakdown treatment, has low thermionic activity. Photoconduction, photoemission, and reflection measurements are made at several coating temperatures between 300°K and 700°K. It is then activated by heating the cathode to approximately 1200°K and drawing emission current. After flashing more getter to clean up any additional gas generated during this treatment, the cathode is cooled and the observations repeated. To obtain a measure of the state of activation, the emission current, taken at the point at which it departs 20 percent from the $\frac{3}{2}$ power voltage law,[6] is determined as a function of temperature, before and after activation.

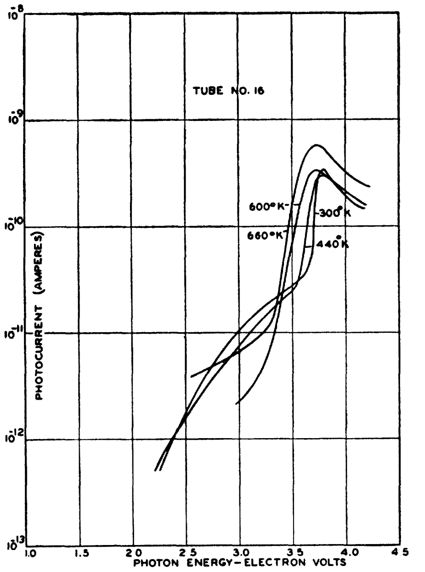

FIG. 5. Photoconductivity in unactivated BaO.

Observations on some twenty tubes have shown good agreement among themselves. The majority of the results presented here were taken on one of these tubes and were selected because a more extensive set of observations was made with this tube than with most of the others. Studies on barium oxide, as observed before any attempt at activation, are described in the following three sections.

III. REFLECTION

Figure 3 shows representative curves of spectral reflection from a barium oxide coating plotted against the quantum energy of the incident radiation. Following a gradual reduction in reflection as the energy increases, there is an abrupt drop corresponding to the characteristic absorption edge. A threshold for this is obtained, as indicated on the curve, by extrapolating the curve from both sides of the knee and finding the intersection of these extrapolated curves. For BaO at room tem-

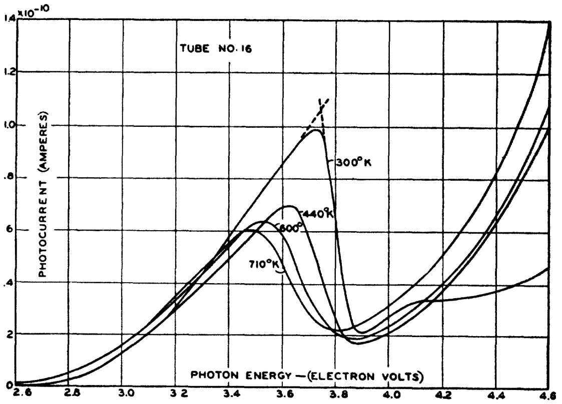

FIG. 6. Photoelectric emission from unactivated BaO.

---

[6] Hannay, McNair, and White, J. Appl. Phys. 20, 669 (1949).

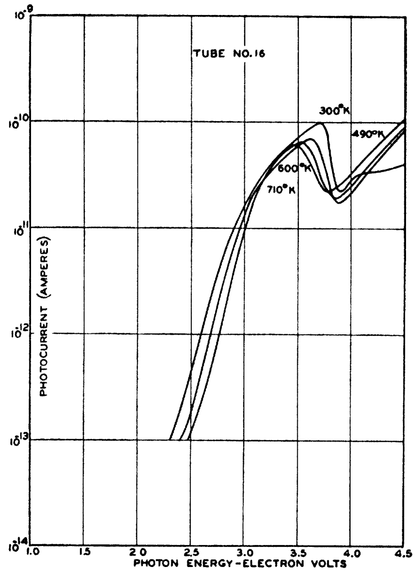

FIG. 7. Photoelectric emission from unactivated BaO.

perature, a threshold value of 3.7 ev is obtained. This is in satisfactory agreement with the value 3.8 ev found by Tyler[3] from absorption measurements on both single crystals and evaporated films of BaO. As the temperature of the oxide is increased, the knee of the curve becomes more rounded and the threshold is displaced towards lower quantum energies.

IV. PHOTOCONDUCTIVITY

Representative curves showing spectral distribution of photoconductivity are shown with the current plotted linearly in Fig. 4 and in a logarithmic form in Fig. 5. The large rise in current, extrapolated as shown in Fig. 4, shows a threshold at the characteristic absorption edge of BaO. As the temperature increases, the photoconduction current shows a small increase in magnitude and at the same time the threshold is displaced towards lower energies, corresponding to the same displacement noted for the reflection curves.

V. PHOTOEMISSION

Figures 6 and 7 show the spectral distribution of external photoelectric emission from a representative BaO specimen. The shape of the curves suggests a continuous rise in emission with increasing quantum energy, on which is superimposed a process which reduces this emission, commencing sharply near the absorption edge and becoming less effective towards higher energies. This appears to be similar to the effect described by Taft and Dickey[4] for the photoemission from thin films of Ba and BaO and to be caused by a reduction of the electric vector of the radiation in the neighborhood of the BaO surface. This electric vector, which is the resultant of the incident and reflected field vectors, suffers a large reduction in the region of an absorption edge, where the index of refraction takes on abnormally large values. If the threshold for this emission reduction is defined as the intersection of the prolongation of the curves before and after the reduction, as indicated in Fig. 6, this is again found to lie close to the characteristic absorption edge for BaO.

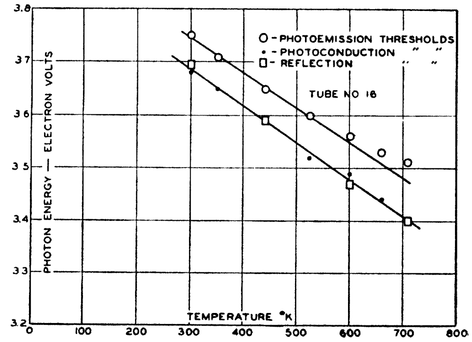

FIG. 8. Temperature dependence of threshold energies.

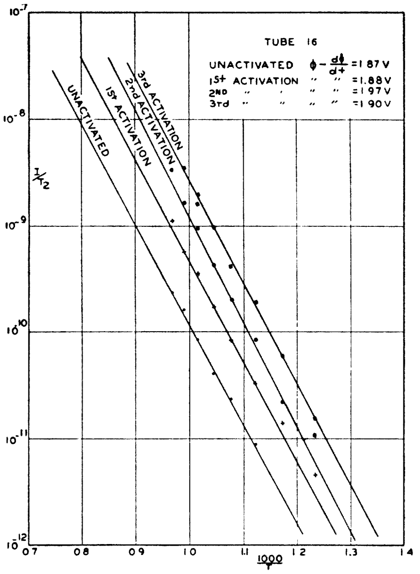

FIG. 9. Richardson plot.

The threshold values of photon energy for reflection, photoconduction, and reduction of photoemission are plotted against temperature in Fig. 8. To a good approximation, these points, over the range from 300°K to 700°K, can be represented by straight lines having a slope corresponding to a threshold displacement of 7×10^{-4} ev per degree.

The low energy tails of photoemission curves have often been fitted to Fowler plots. This was tried for our measurements, but the fit obtained was very poor. This does not seem especially significant, since present semiconductor theory does not lead one to expect such a fit.

VI. ACTIVATION

After observations were made of reflectivity, photoconductivity, and photoelectric emission for the barium oxide, the cathode was activated by heating and drawing emission current. At each step of the activation, the emission current was measured as a function of the cathode temperature and Richardson plots were made. These plots, for four stages of activation, are shown in Fig. 9. It is notable that the change in slope during the course of the activation is small, as shown by the corresponding values[7] for $(\phi - Td\phi/dT)$, and that the total change in thermionic emission from the initial to the final state of activation is only about a factor of 20. Since the final state gives emission comparable with that for a well-activated BaO cathode, it is indicated that the cathode breakdown treatment used actually produces some activation, as would be expected.

Figures 10 and 11 show photoconductivity and photoemission as measured for the same specimen at the same stages of activation. In both of these a considerable change takes place during the second activation treatment, with relatively smaller changes before and after this stage. The thermionic emission data of Fig. 9 do not show a similar progression.

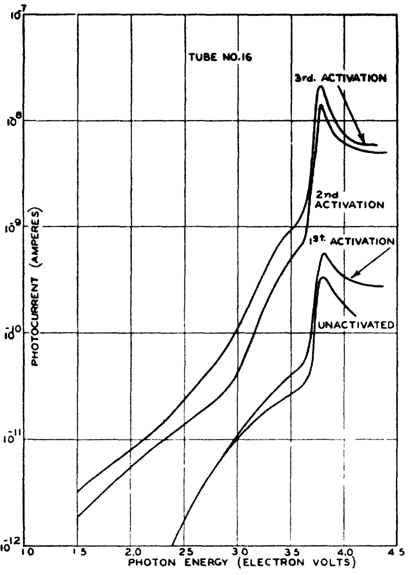

FIG. 10. Dependence of photoconductivity on activation.

Photoconductivity shows a general increase in magnitude with activation. Photoemission, on the other hand, shows a marked change in spectral distribution when activated. A very large increase is found in the region of high absorption. In the low energy region, the photoemission becomes sensitive to the treatment of the specimen, as is shown in Fig. 12. The currents observed in this region are small if the cathode is heated a few hundred degrees and then cooled in the dark. Irradiation of the cold oxide with light in the region of characteristic absorption (>3.7 ev) causes the photoemission measured subsequently in the low energy region to show a large increase with a peak at 2.5 ev. This high photoemission decays slowly, with a time constant of the order of a day. These changes are reproducible, and the low energy photoemission may be increased by short wavelength irradiation or decreased by annealing, at will. This phenomenon has not been observed in the case of photoemission from the BaO before activation, nor in any of the photoconductivity measurements.

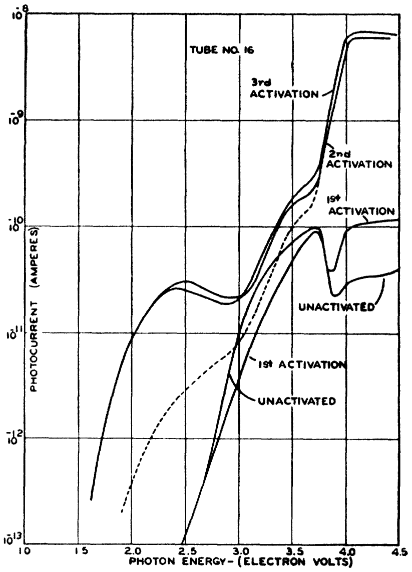

FIG. 11. Dependence of photoelectric emission on activation.

In recording the curves shown in Fig. 11, the BaO surface was in every case exposed to short wavelength illumination before the curves were taken, and the low energy portions correspond to the curve of Fig. 12 for the irradiated oxide. For comparison, the dashed curve

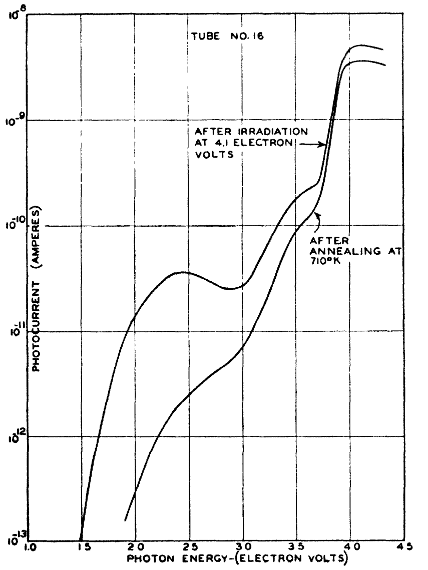

FIG. 12. Effect of irradiation and annealing on photoemission.

---

[7] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 402.

in Fig. 11 has been drawn in to indicate the response that would be expected for the second and third activation stages if the specimen had been properly annealed.

In the activated state, the changes in photoconductivity curves with temperature are similar to those observed for the unactivated state. In the case of photoemission, again, the changes are markedly different, as shown in Fig. 13. A small increase in temperature produces a very rapid decrease in the photoemission in the high quantum region. Between 500°K and 600°K, this goes through a minimum, and at higher temperatures the photoemission in the region above 3 ev rises again. In Fig. 13, as in Fig. 11, a dashed curve has been drawn in to indicate the response expected for the oxide at 300°K in a properly annealed condition.

The reflectivity curves are substantially unchanged by the activation.

VII. DISCUSSION

The interpretation of these observations in terms of an energy level diagram for barium oxide is not yet wholly satisfactory, but a number of inferences may be drawn. A representation of such an energy level diagram is given in Fig. 14. It is assumed that a number of both donor and acceptor levels are located in the gap between the bottom of the conduction band and the top of the filled band.

It may be assumed that in the inactive state, the number of donor sites is considerably less than the number of acceptor sites. The Fermi level appropriate to this condition should be comparatively low and the thermionic emission very small. The activation process is regarded as forming a large number of donor sites. When the number of these begins to exceed the number of acceptors, the number of occupied donors will become appreciable, and the Fermi level will rise to a position in the neighborhood of the donors. Further activation will increase rapidly the number of occupied donor sites, but the Fermi level will rise only slowly. The Richardson plots indicate that, in the case of our specimens, the "unactivated" state already corresponds to a density of donors somewhat in excess of the density of acceptors present.

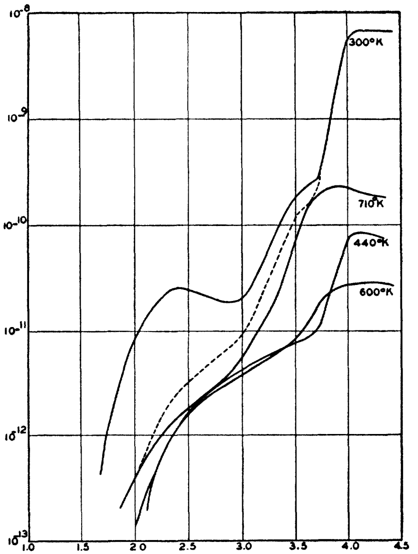

FIG. 13. Photoemission from activated BaO—temperature variation.

Apker, Taft, and Dickey[5] have found that the photoemission from BaO shows a large increase setting in around 5.0–5.2 ev, and it appears probably that this represents the depth V_f of the top of the filled band below vacuum potential. Our light source did not permit measurements for confirmation of these observations.

The large absorption setting in at about 3.7 ev must be ascribed to transitions in which electrons are raised from the top of the filled band, in view of the large absorption coefficient ($\sim 10^5$/cm) found by Tyler. Since the photoconductivity measurements also show a large increase starting at this point, the transition must be either to the conduction band directly, or else to states lying sufficiently close to the base of the conduction band that thermal transfer into the band has a high probability at room temperature. The direct transfer seems unlikely, among other reasons, because this would call for an improbably large value for the electron affinity (1.3–1.5 ev), for which values in the range 0.7–0.9 ev seem to be currently favored.

The band separation may be taken to be a little more than 3.7 ev, and the temperature variation data indicate that this band separation decreases at the rate of 7×10^{-4} ev per degree C. This rate of change of band separation is in reasonably good agreement with the well-known displacement of absorption bands, usually taken to be 1A per degree C.

In the case of photoelectric emission from activated BaO, there is a conspicuous increase for photon energies just above the 3.7-ev absorption edge. Both our photoconductivity studies and observations made by Apker[8] on energy distribution of photoelectrons indicate that there does not exist any concentration of electrons in states at this depth below vacuum potential. A possible explanation has been advanced by Apker which assumes that photoemission in this region is largely caused by interaction between excitons and electrons in the donor sites. According to this suggestion, the high energy incident photons create excitons near the surface of the crystal. An exciton may dissociate thermally to form a conduction electron, or it may recombine, or it may encounter an electron in a donor site near the surface and, by transfer of its excitation energy, cause this electron to be emitted from the surface. Since the high absorption coefficient in this region indicates a high density of excitions near the surface, the probability of electron release by this process might be expected to be higher than for the direct photoelectric process.

---

[8] L. Apker (private communication).

A rise in temperature should increase the probability that an exciton would dissociate thermally, with corresponding increase in photoconductivity, as has been observed, before it encounters an electron at a donor site. Hence, the photoemission in the absorption region should decrease with increasing temperature, as is observed. The subsequent rise in photoemission for temperatures above 600°K may perhaps be accounted for by assuming that this represents thermionic emission of electrons which reach the conduction band by exciton dissociation.

The 2.5-ev peak in the photoemission from activated BaO, caused by irradiation in the absorption region, indicates the presence of a number of donor sites at this depth below vacuum potential, most of which are normally unoccupied but which may be filled by electrons from the conduction band. The large rise beyond 3.7 ev, and its smaller dependence on irradiation, argues the presence of larger number of occupied sites, which may be distributed down to at least 3.7 ev below vacuum potential. On the other hand, in the case of photoemission from the unactivated BaO, there is no sharp rise for photon energies above 3.7 ev, nor is there any evidence of a peak in the neighborhood of 2.5 ev. This would seem to indicate a very low density of donor sites, whether occupied or not, in the unactivated state. This conclusion, however, is hardly compatible with the observed uniformity of slope of the Richardson plots.

A detailed interpretation of the photoemission data is rather hazardous until a determination can be made as to which of the features are characteristic of the volume properties of the BaO crystals as distinguished from those which are representative of the surface conditions existing.

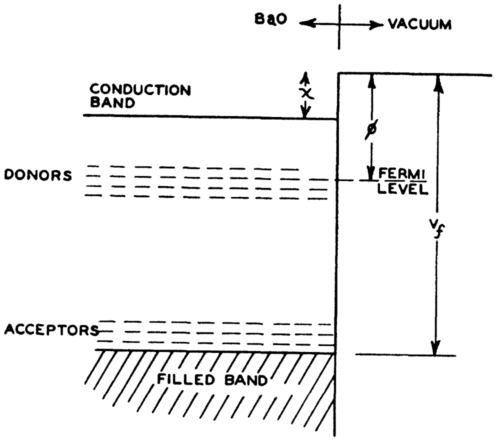

FIG. 14. Energy level diagram for BaO.

Photoconductivity induced by photons with energy less than 3.7 ev is presumably due to electrons raised to the conduction band from donor or acceptor sites. The increase observed on activation may be largely accounted for by the increased density of occupied donor sites, which also produce the rise in thermionic emission. In addition, there may be an increase in mobility of electrons in the conduction band, resulting from a reduction of trap density. However, since this latter would affect equally the photoconductivity in all spectral regions, while the increase in the absorption region is always proportionately larger than that in the low energy tail, some further mechanism is required. This could be provided, on the exciton hypothesis, by the assumption that the probability of exciton recombination before thermal dissociation is relatively large in the unactivated state and that it is reduced by activation.

The authors wish to express their indebtedness for numerous suggestions and discussions to Professor L. P. Smith and to their other colleagues at RCA Laboratories. In addition, they have profited from discussions with Dr. C. Herring and others of Bell Telephone Laboratories, and with Dr. L. Apker, Dr. W. W. Tyler, and others at General Electric Research Laboratories