

Exciton-Induced Photoemission from BaO near 80°K*

E. TAFT, H. PHILIPP, AND L. APKER

General Electric Research Laboratory, Schenectady, New York

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This paper reports a new photoelectric study of BaO at 80°K. Special attention was devoted to the spectral region near $h\nu=4$ ev, where Zollweg and Jahoda have found four peaks in the optical absorption. When BaO contains electron donor states lying less than 2 ev below the vacuum, these peaks show up clearly at 80°K in the spectral distribution of the photoelectric yield. The effect appears similar in character to exciton-induced photoemission from alkali halides. In BaO, the phenomenon furnishes a particularly sensitive means of studying the weak absorption peak at 3.8 ev, which can give rise to photoemission at photon energies as low as 3.3 ev. This is probably the source of the unexpected slow electrons previously observed by Philipp in energy distributions. Electron donor states giving rise to photoelectric thresholds as small as 0.8 ev were seen during the present studies.

INTRODUCTION

ZOLLWEG¹ and Jahoda² have found structure in the fundamental optical absorption and reflectivity of BaO near $h\nu=4$ ev.³ Sharp maxima in the optical absorption are similar in some ways to the fundamental absorption peaks of alkali halides,^{4,5} in which the peaks of lowest photon energy are associated with non-conducting excited states ascribed to exciton formation. Optical energy absorbed in these exciton peaks can be transferred to *F* centers or to other electron donor centers present in the crystal. The centers are ionized and exciton-induced photoemission results.⁶

This report describes new photoelectric experiments on BaO. Special attention was devoted to the absorption peaks described by Zollweg and by Jahoda. In order to detect exciton-induced photoemission, electron donor centers were introduced, and the measurements were made at 80°K. The results are compared with those for alkali halides.

EXPERIMENTAL DETAILS

Phototubes with cylindrical collectors were used.⁷ The BaO emitters were formed by decomposing

Mallinckrodt BaCO₃ on Pt, Ni, or Ta ribbons in the usual manner.⁸ The ribbon supports were vertical Kovar tubes (8-mm diameter) which were sealed through the wall of the tube envelope. Enough current could be passed through these to heat the ribbon electrically to temperatures above 1200°C. Alternatively, the Kovar tubes could be filled with liquid nitrogen in order to cool the emitter to temperatures within a few degrees of 80°K. The phototube windows were made of fused quartz. Small evaporators mounted inside the collector served in some cases as sources of Mg to introduce donor levels in the BaO. Donors were also formed by heat treatment like that used in activating thermionic cathodes.⁸ Other experimental details are given in previous papers.^{6,7}

DISCUSSION OF RESULTS

Figure 1 shows the spectral distribution of the photoelectric yield near 80°K from a typical BaO sample containing donors. Several different phenomena occur in different spectral ranges. Proceeding from low photon energy toward high, we shall treat them in sequence.

First, a very small photoelectric yield appears at a threshold photon energy just below 1 ev. It has a form characteristic of direct ionization.⁶ The electron energy level involved is surprisingly shallow. It is apparently populated only at low temperature. Thus, this yield does not appear if the emitter is warmed to 300°K. As judged by the photoelectric yield at $h\nu\sim 1.4$ ev, for example, the concentration of these centers may be increased at 80°K by irradiating the emitter at higher photon energies (especially in the region of fundamental absorption above 4 ev). The centers disappear slowly in the dark at 80°K. In the course of a day, the photoelectric yield at $h\nu=1.4$ ev decreases from 10^{-6} electron/incident photon to less than 10^{-7} . During the irradiation that is necessary to measure the yield, the centers are of course destroyed more rapidly.

Varenna Conference, 1957 [Suppl. Nuovo cimento 7, 157 (1958)]; *J. Chem. Phys.* 21, 849 (1953).

⁷ For a sketch of a related design, see L. Apker and E. Taft, *Phys. Rev.* 81, 698 (1951).

⁸ See, for example, H. R. Philipp, *Phys. Rev.* 107, 687 (1957).

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¹ R. J. Zollweg, *Phys. Rev.* 97, 288 (1955); see also *Bull. Am. Phys. Soc. Ser. II*, 2, 342 (1957); G. A. Saum and E. B. Hensley, *Bull. Am. Phys. Soc. Ser. II*, 2, 343 (1957); K. Takayawa and T. Tomotika, *J. Phys. Soc. Japan* 9, 996 (1954); K. Okumura, *Phys. Rev.* 96, 1704 (1954).

² F. C. Jahoda, *Phys. Rev.* 107, 1261 (1957).

³ W. W. Tyler and R. L. Sproull, *Phys. Rev.* 83, 548 (1951), showed in earlier work that the absorption constant rose rapidly to values near 10^5 in this region. See also E. A. Taft and J. E. Dickey, *Phys. Rev.* 78, 625 (1950).

⁴ See W. Martienssen, *J. Phys. Chem. Solids* 2, 257 (1957) and cited references to earlier work; Hartman, Nelson, and Siegfried, *Phys. Rev.* 105, 123 (1957); K. J. Teegarden, *Phys. Rev.* 108, 660 (1957); E. A. Taft and H. R. Philipp, *J. Phys. Chem. Solids* 3, 1 (1957).

⁵ For recent theoretical references, see A. W. Overhauser, *Phys. Rev.* 101, 1702 (1956); R. L. Dexter, *Phys. Rev.* 108, 707 (1957); J. J. Hopfield, *Bull. Am. Phys. Soc. Ser. II*, 3, 125 (1958); J. R. Nelson and J. J. Hopfield, *Bull. Am. Phys. Soc. Ser. II*, 3, 126 (1958).

⁶ H. R. Philipp and E. Taft, *Phys. Rev.* 106, 671 (1957) and cited references. See also, D. L. Dexter, in *Proceedings of the*

Although the center responsible for this yield was not identified in this work, the energy level is an interesting one. The behavior is somewhat like that of F' centers in alkali iodides, but the level is not so deep. (One notes that the threshold for this yield from BaO is almost as small as that for emission from silver oxide-cesium surfaces). Conceivably, a surface level may be involved. In order of magnitude, 10^{12} occupied levels per cm^2 could produce a yield this large.⁹ On the other hand, if the donor is in bulk BaO, the level presumably lies below the bottom of the conduction band. If this band is not distorted by electric fields near the surface, the electron affinity of the BaO must be less than the threshold value, which itself is below 1 eV.¹⁰ This result is consistent with a suggestion by Hensley¹¹ that the electron affinity of BaO is less than 1 eV.

In Fig. 1, the yield shows a second threshold near 1.6 eV. This is due to direct ionization of donors that arise when the BaO is activated by heat treatment. Again they were not identified in this work, but they are apparently the same centers as discussed by Philipp,⁸ and they appear along with high thermionic emission. They are stable above 500°K. (Irradiation of BaO near room temperature can produce electron donor centers with about the same photoelectric threshold energy, but these are not stable at higher temperatures). The photoelectric yield from these donors has a plateau value near 2×10^{-4} electron per incident photon. This could arise in a concentration of occupied surface levels 10^{14} cm^{-2} .⁹ We think it more likely, however, that this yield arises from levels in the volume. Following the rough estimate made for F centers in KI,⁹ one concludes that a concentration of order 10^{20} cm^{-3} in a layer 10^{-6} cm thick near the surface could give such a yield.

When these donors are present in BaO, the yield rises sharply at about $h\nu = 3.3$ eV. This rise is not due to direct ionization. It reaches a plateau (and in some cases, a peak) near 3.8 eV, where Zollweg and Jahoda both noticed evidence for a weak absorption peak. This structure shows up more clearly in photoemission than in absorption. It is conceivable that it is analogous to β -band or similar perturbed fundamental absorption in alkali halides, which can lead to a type of exciton-induced photoemission.¹² If it is due to absorption in the ideal lattice, it is surprisingly broad. In any event,

⁹ Apker, Taft, and Dickey, *Phys. Rev.* **74**, 1462 (1948); **79**, 964 (1950).

¹⁰ This conclusion also holds if the conduction band rises toward the surface (that is, if the BaO is less strongly n type at the surface than in the bulk). If the conduction band rises away from the surface (if the surface is more strongly n type than the bulk), one must be more cautious. The threshold may then be less than the electron affinity, but the yield should then rise with $h\nu$ more slowly than in the other case.

¹¹ E. B. Hensley, *J. Appl. Phys.* **23**, 1122 (1952); see also reference 16.

¹² E. Taft and L. Apker, *J. Chem. Phys.* **20**, 1648 (1952).

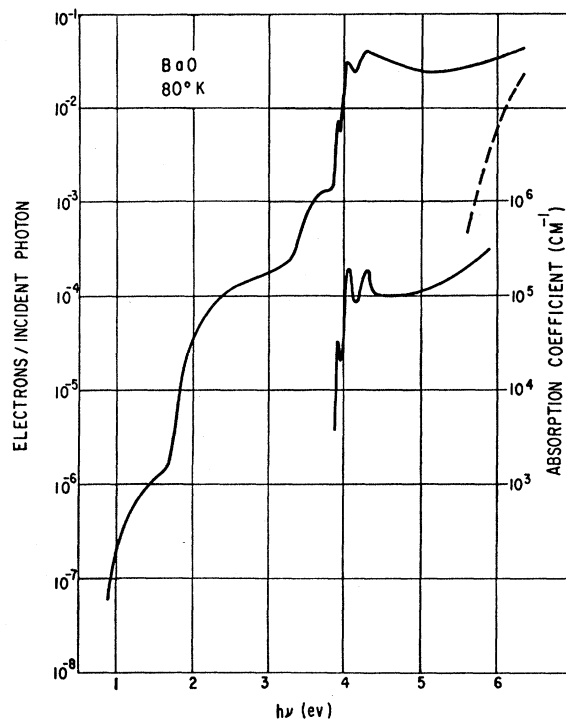


FIG. 1. Spectral distribution of the photoelectric yield from a typical sample of BaO containing donors (upper solid curve). The dashed line shows data on a relatively pure sample, for which the photoemission arises only in the valence band. The lower solid curve shows the optical absorption of a well-annealed thin film of BaO (ordinate scale at the right) measured with the same monochromator. Absolute values of absorption coefficient were estimated to be within a factor of three of those given by Zollweg; they have been set equal to Zollweg's values on the scale above.

the peak position agrees with that deduced by Zollweg and Jahoda.

This absorption is doubtless the source of the surprisingly large yield of slow photoelectrons found by Philipp for values of $h\nu$ near 3 eV.^{8,13} These electrons had an energy distribution characteristic of exciton-induced emission, which, at the time that this work was done, was quite unexpected at such low photon energy.

The sharp peaks at 3.91, 4.05, and 4.30 eV are coincident in position and consistent in magnitude,¹⁴

¹³ Evidence for this same type of emission may be found in spectral distributions given by H. B. DeVore and J. W. Dewdney, *Phys. Rev.* **83**, 805 (1951).

¹⁴ For the carefully annealed films used by Zollweg and for the single crystals used by Jahoda, the peak at 4.05 eV is stronger than at 4.31. For less carefully annealed films, the peak at 4.05 is weaker. The photoemission from BaO made by pyrolysis of BaCO_3 shows structure that resembles the absorption in the latter films. One notes also that for alkali halides, at least, the photoelectric yield rises more slowly than the optical absorption constant when the latter exceeds about $2 \times 10^5 \text{ cm}^{-1}$ (presumably because photoelectrons escape from depths of order $5 \times 10^{-6} \text{ cm}$). Both photoemission and optical absorption measurements made on thin films of BaO in a tube like that of reference 7 indicate that the temperature dependence of the exciton peak positions is about $10^{-4} \text{ eV per degree}$. There is an indication that the higher energy peaks move slightly toward higher energy as temperature

with the optical absorption peaks of BaO. It is most unlikely that they are a trivial consequence of structure in the reflectivity of BaO, since they would then have quite different locations and magnitudes. Thus, we interpret these peaks as due to exciton-induced photoemission. One notes that this process is about 100 times more efficient than direct ionization at the concentration of donors used in the experiment of Fig. 1. The photoelectric yields are large, rising above 0.01 electron/incident photon. As in the case of alkali halides,⁶ the donors are probably so numerous and close together that either resonant transfer (with a range of about 50 Å) or exciton migration could account for the observed yields.⁶ This exciton-induced emission (as well as that at 3.8 eV) appears only when there are donor centers lying less than 2 eV below the vacuum, as judged by the threshold for direct ionization. For donors lying farther below the vacuum than this, the yield exhibits a decrease, rather than an increase, as $h\nu$ enters the region of fundamental absorption.^{8,13} Thus, we conclude that while about 4 eV is required to create the excitons in BaO, only about half of this is transferred to the electrons in donor centers when they are ionized. This is similar to the situation for *F* centers in alkali iodides.

To facilitate discussion of yields from BaO at higher photon energies, we first restate the present situation for alkali halides. Just beyond the first peak in the photoemission from alkali iodides, there is a small peak (as yet of unexplained origin) near an optical absorption edge which has been attributed to interband transitions.¹⁵ Beyond the edge, the optical absorption shows a plateau, but the photoemission decreases.

increases; the peak at 3.8 eV may move slightly toward lower energies (thus in photoemission it is better resolved as a peak at room temperature).

¹⁵ E. A. Taft and H. R. Philipp, *J. Phys. Chem. Solids* **3**, 1 (1957).

Optical absorption peaks lying at higher energies than the edge do not show up in the photoemission. At an energy about 1 eV above the edge is the threshold for photoemission from the valence band (except in the case of CsI, for which the threshold is practically coincident with the edge).

For BaO at 80°K there are four optical absorption peaks, as follows: a weak, broad one at about 3.8 eV; a very sharp one at 3.91 eV (width, 0.02 eV); two broader ones at 4.05 eV (width, 0.07 eV) and 4.30 eV (width, 0.22 eV). These are followed by a plateau absorption; if this is due to exciton absorption bands they are not resolved. Finally, just above $h\nu=5$ eV is a rapid rise in absorption which has been ascribed to interband transitions.¹⁶ Continuous absorption due to indirect interband transitions may set in at even lower energies, but it is not easy to tell just where it begins. One may consistently explain the optical absorption data, for example, as due to four peaks followed by continuum that begins at about $h\nu=4.5$ eV.

In any event, all four peaks show up clearly in the photoemission. If we argue by analogy with alkali iodides, this suggests that none of these peaks is superposed on strong continuum due to interband transitions. We can not be sure, however, that the analogy is reliable in this case.

Photoemission from the valence band begins near 5 eV.¹⁷ (It becomes large enough at about 5.5 eV in Fig. 1 to produce a rise in the yield.) If we subtract the electron affinity of BaO from this threshold value of 5 eV, we get the threshold for indirect interband transitions. An electron affinity less than 1 eV and an interband optical absorption threshold above 4 eV, as mentioned above, are consistent with the data of Fig. 1.

¹⁶ J. A. Krumhansl, *Phys. Rev.* **82**, 575 (1951); A. Morita and C. Horie, *Science Repts. Tohoku Univ.* **26**, 260 (1952).

¹⁷ Apker, Taft, and Dickey, *Phys. Rev.* **84**, 508 (1951).