On the Photoelectric Emission and Energy Structure of BaO*

L. APKER, E. TAFT, AND J. DICKEY

General Electric Research Laboratory, Schenectady, New York

(Received July 16, 1951)

Spectral distributions of the photoelectric yield and energy distributions of the photoelectrons were obtained for BaO surfaces made in widely different ways. A small and variable yield for $h\nu < 5$ ev was attributed to unidentified imperfections. At the optical absorption edge, there was an effect much like the exciton-induced photoemission in alkali halides. At $h\nu \sim 5$ ev, an abrupt rise in the yield was ascribed to emission from an occupied band of electron states with an upper edge 5 ev below the vacuum level. Energy distributions were consistent with this interpretation.

1. INTRODUCTION

SOME time ago we began a photoelectric investigation of BaO. It became apparent very early that the problem was complex. There was little basic photoelectric work on ionic crystals (especially divalent ones) to serve as a guide. We therefore turned our attention to simpler materials, the alkali halides. Some of the subsequent results have been reported.[1] They form much of the basis for the point of view taken here.

This paper describes the work on BaO. The main conclusion offered is that a photon energy near 5 ev is required to raise an electron from the occupied energy band of BaO to the vacuum level. Various phenomena observed at lower photon energies are briefly mentioned.

2. EXPERIMENTAL TECHNIQUES

This report is based on observations of several hundred surfaces. They were of three general types, prepared in the following ways: (1) Evaporated films of
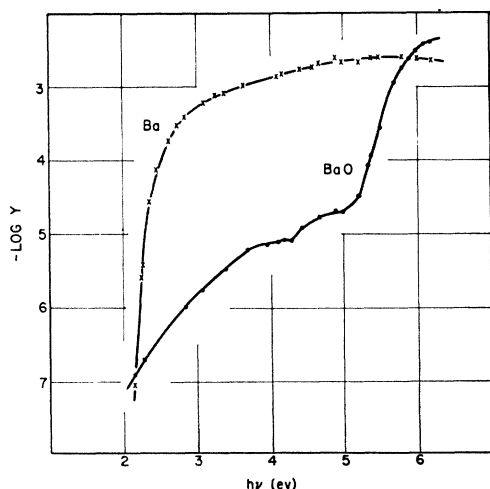

FIG. 1. Spectral distribution of the photoelectric yield Y (in electrons/quantum) for metallic Ba and for BaO formed by oxidizing this same sample.

---

[1] L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951).

Ba metal were oxidized in sealed-off phototubes. Heated silver tubes[2] admitted pure O_2 until BaO was formed; excess O_2 was removed with getters (usually W or Ta wires flashed at high temperatures). (2) BaO formed by pyrolysis of $BaCO_3$ was evaporated from pure Pt ribbons.[3] (3) BaO surfaces were formed directly by pyrolysis of $BaCO_3$ on various substrates.

The phototubes were of several different varieties, most of which have been described before:[4] (a) Spherical collectors with interchangeable emitters permitted simultaneous measurements of contact potentials and photoelectron energy distributions at 300°K as well as at somewhat higher temperatures; (b) Cylindrical diodes with central emitters were used to determine spectral distributions of photoelectric yields at 300°K and at slightly higher temperatures; (c) Diodes like those used in alkali halide work[1] furnished spectral distributions at 300°K and at ~85°K.

Other experimental details have been given previously.[4]

3. SPECTRAL DISTRIBUTION OF THE PHOTOELECTRIC YIELD

Perhaps the most interesting way to observe the frequency variation of the photoelectric emission from BaO is to measure a Ba metal film and then to oxidize it (method 1, Section 2). Data obtained in this way with a phototube of type (a) in Section 2 are shown in Fig. 1. The threshold of the Ba metal is near 2.3 ev, and the yield follows the usual trend for a metal of this sort. When the metal is converted to BaO (at ~600°K), drastic changes occur in the photoemission. For $h\nu$ between 3 and 5 ev, the yield drops by a factor of 100 or more, depending on the completeness of the oxidation. For $h\nu$ between 1 and 2 ev (i.e., in a region where no emission is observable from pure Ba metal), a very small yield may appear. A rise in this yield may occur near 3.8 ev, the absorption edge of BaO.[5] (In Fig. 1

[2] J. B. Taylor, Rev. Sci. Instr. **6**, 243 (1935).

[3] We are grateful to George E. Moore of the Bell Telephone Laboratories for the pure Pt used here. (See Phys. Rev. **77**, 247 (1950).) The $BaCO_3$ was Mallinckrodt Ultra Pure.

[4] See reference 1. Also: Apker, Taft, and Dickey, Phys. Rev. **74**, 1462 (1948); **73**, 46 (1948). A diagram of one type of tube is given in a review by J. A. Becker, Elec. Eng. **68**, 937 (1950).

[5] W. W. Tyler, Phys. Rev. **83**, 548 (1951); E. Taft and J. Dickey, Phys. Rev. **78**, 625 (1950). This rise in the yield from BaO

this effect is not clear-cut, but a slight rise is nevertheless evident just above 4 ev.) As $h\nu$ increases above 5 ev, the yield rises abruptly to values near 10^{-2} electron/quantum, considerably higher than the maximum yield of Ba metal.

Examples of this same general behavior are shown in Fig. 2 for BaO specimens made in other ways. The abrupt rise at 5 ev has been characteristic of all our samples, regardless of the method used to make them. In contrast, the behavior for $h\nu < 5$ ev depends on the way in which the sample was made and may also depend on irradiation history.[6]

We have interpreted these results as follows: The rise at 5 ev we believe to be due to photoelectrons ejected from the occupied band of BaO. Thus, the top of this band lies about 5 ev below the vacuum level.

The small yield for $h\nu < 5$ ev we attribute to photoelectric emission from impurities and imperfections, probably of several kinds. Permanent centers (presumably electrons in vacancies) may be associated either with excess Ba or with foreign atoms in the material. Metastable centers may be produced during irradiation, particularly for $h\nu > 3.8$ ev;[6] these may be due to traps either normally in BaO or associated with foreign atoms. If the time required for metastable centers to form or to decay is long enough, the effect may be isolated easily and treated independently. We have observed times as short as three seconds, however, in certain evaporated films. In such cases, separate treatment of metastable centers was not convenient in our work.

The rise in the yield at $h\nu \sim 3.8$ ev we believe to be caused by exciton-induced photoelectric emission from the centers mentioned above. In some samples, metastable centers which formed rapidly during the measurement also contributed to the effect. Other structure near this edge may arise because of the onset of opacity in the film and because of frequency-dependent optical reflection at the surface.[1] The important point here is that this feature in the yield is not a primary effect. It may not be considered as due to occupied energy levels beginning 3.8 ev below the vacuum level. It is indicative only of the onset of optical absorption and related processes.

Since a small yield in many samples is observable for $h\nu \sim 1.5$ ev, we conclude that occupied impurity levels may lie only a little more than 1 ev below the vacuum

FIG. 2. Spectral distributions for BaO made as follows: (a) by pyrolysis of $BaCO_3$; (b) by oxidation of Ba metal; (c) by evaporation of BaO from a Pt ribbon. The thickness of the last sample was of the order of 10^{-6} cm. The structure near the absorption edge at 3.8 ev frequently does not appear for such thin samples, perhaps because of exciton destruction at surfaces.

level. As Herring[7] has emphasized, the Franck-Condon principle must be kept in mind in considerations like these. We remember, therefore, that the photoelectric thresholds of these BaO samples may not be correlated in any simple way with thermionic work functions or with contact potentials. Further, conditions in the material may deviate from equilibrium. In similar work on RbI,[8] discrepancies with these origins amounted to more than 1 ev. In BaO, they appear to be less.

The form of the spectral distribution in this region ($h\nu < 3.8$ ev) varied considerably in our work. It was evident that the impurities were not always the same and that their concentration varied markedly. (It should be noted here that we are not considering impurity densities comparable with those in activated BaO cathodes.)

When the temperature is reduced to $\sim 85°K$, the yield for $h\nu < 5$ ev sometimes increases when rapidly-formed metastable centers attain a higher concentration during the measurement. The rise in the spectral distribution at $h\nu \sim 3.8$ ev retains its location, however, to within 0.1 ev. This agrees with the temperature independence of the optical absorption as measured by Tyler.[5] While there is an indication that the abrupt rise in the yield near 5 ev becomes slightly steeper,[9] this feature shifts by less than 0.1 ev also.

4. ENERGY DISTRIBUTION OF THE PHOTOELECTRONS

Figure 3 shows current-voltage characteristics for a typical BaO sample made by oxidizing Ba metal in a

was noticed previously by H. B. DeVore and John W. Dewdney, Phys. Rev. 83, 805 (1951), to whom we are indebted for discussions of this subject. Tyler's data show another increase in the optical absorption coefficient just above 5 ev. As pointed out below, the photoemission rises abruptly near this same point. At the present stage of our knowledge, we see no connection between these two effects, and the agreement is interpreted here as coincidental.

[6] J. Dickey and E. Taft, Phys. Rev. 80, 308 (1950). Extensive measurements have been made on activated samples by B. D. McNary, Phys. Rev. 81, 631 (1951), to whom we are indebted for an advance copy of his manuscript. If the sample is pure, this effect is large only in the region of fundamental optical absorption, $h\nu > 3.8$ ev. A less prominent effect may be obtained for smaller $h\nu$ if there is optical absorption outside the fundamental range.
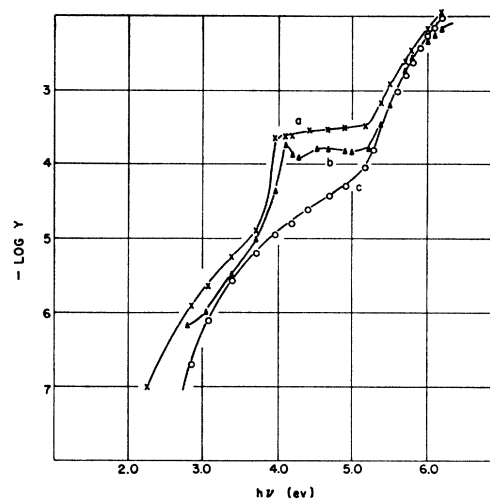
[7] C. Herring, private communication; Phys. Rev. 73, 1238 (T) (1948).

[8] L. Apker and E. Taft, Phys. Rev. 82, 814 (1951).

[9] Such an effect could be due to the phenomena discussed by H. B. Callen, Phys. Rev. 79, 533 (1950).

spherical tube of type (a) in Section 2. The outstanding effect observed is that the "stopping potential" V_0' for the BaO is roughly 3.5 ev more positive than the "0°K stopping potential" V_0 for the auxiliary interchangeable metals. Thus the Fermi level in the BaO lies above the top of the occupied band by this same 3.5 ev.[10] The saturation point V_s at ~ 3.1 v indicates that the work function of this sample is about 1.6 ev.[11] Within the experimental uncertainties in these results (perhaps as much as 0.2 ev), the data are consistent with the conclusion drawn above: namely, that the occupied band of energy states lies 5 ev below the vacuum level.

Normally the current-voltage characteristic for $h\nu = 5.8$ ev showed no significant change when the emitters were heated to 600 or 700°K. For thoroughly oxidized Ba, however, the stopping potential V_0' became more negative by as much as 1 ev. Thus, $V_0' - V_0$ decreased from 3.5 ev to about 2.5 ev as shown in Fig. 3. This result would be expected if the Fermi
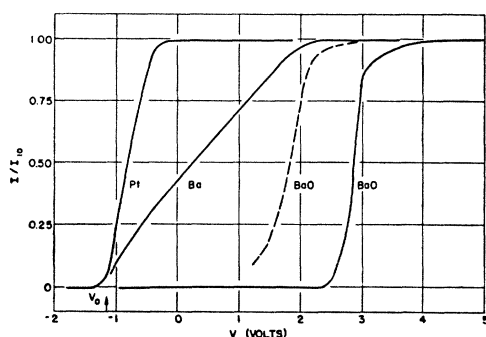

FIG. 3. Current-voltage characteristics for BaO and two typical metals; $h\nu = 5.80$ ev, $T = 300$°K. The dotted curve shows data on a vigorously oxidized sample at $T \sim 650$°K. The point $V_0 = -1.16$ volts corresponds to the Fermi level.

level dropped toward the occupied band when the temperature increased. This is a well-known charac-

---

[10] The symbols used here are the same as in Phys. Rev. **74**, 1462 (1948). See also H. B. Huntington and L. Apker, Phys. Rev. **81**, 321(A) (1951). We assume that equilibrium concepts are meaningful in this case. Thus, we avoid discussing complications like those mentioned in reference 8.

[11] In many cases, samples were non-uniform, and saturation points were not clear-cut. This was a common difficulty also in previous work on alkali halides (reference 8). Since the effect was difficult to eliminate in the case of BaO, the following procedure was sometimes adopted: The metal sleeves which covered the hairpin-shaped emitter support were held several volts more positive than the emitter. (Normally they are held at a potential which just eliminates the stray fields due to the uncontrolled contact potentials.) Under these conditions, retarding-potential measurements may be made in the usual way, but an accelerating field is maintained at the emitter surface. Although a small fraction of the current is diverted to the sleeves, tests with uniform surfaces showed that characteristics were not seriously distorted near the saturation point by this procedure [see, for example, Phys. Rev. **73**, 46 (1948)]. In this case of non-uniform surfaces, the saturation points became more sharp and reproducible. The stray fields due to the relatively large-scale patches then had only a small effect in the presence of the accelerating field at the emitter surface. Patch fields were most troublesome with samples made by methods (1) and (3) of Sec. 3. Evaporated films were much more uniform.

teristic of an N-type semiconductor with a very small concentration of donors. The data given here are consistent with this view, since the shift occurs only fo thoroughly oxidized samples in which donor levels would be expected to exist only in greatly reduced concentration.

The spectral distribution of the yield for the BaO of Fig. 3 was practically the same as in Fig. 1. At 5.8 ev, therefore, all but about 1 percent of the yield arose in the occupied band of energy states. The rest came, of course, from the occupied impurity levels, some of which were as much as 3 ev higher in energy. The contribution of this latter component is not visible on the scale of Fig. 3. It is best seen on a logarithmic plot (of the type used to determine V_0', for example).[10] In such a case, it is still clearly distinguishable from the current arising in the occupied band, since this larger component rises abruptly out of the background. While the impurity yield tends to shift V_0' toward negative voltages, the resulting error is only 0.1 or 0.2 ev and of little consequence here.

Current-voltage characteristics for the impurity component rose to measurable values only when V was several tenths of 1 ev above V_0. (This is quite different from the behavior for a metallic emitter, of course, but is consistent with the Franck-Condon effect mentioned earlier.) They then increased in slope in a more or less regular manner, roughly along an exponential, at a rate near one decade per 1.3 v. This is much like the behavior of the so-called s-group of photoelectrons ejected from F-centers in RbI by exciton stimulation.[8] Since a similar process is possible in BaO for $h\nu > 3.8$ ev, this resemblance is not surprising.

If the impurities were all identical, one would expect photoelectrons ejected by direct ionization ($h\nu < 3.8$ ev) to emerge in a band of energies like the f-group observed for RbI.[8] We have not been able to reproduce such an effect with BaO (although some indications of it appeared in rare cases). There are probably several reasons for this: First, the data of Fig. 1 are not characteristic of a uniform material containing impurities of a single kind. Second, scattering of excited electrons may obliterate the effect if the impurity concentration increases with depth in the sample.[12] Third, patch fields may distort this kind of distribution to such a degree that the accelerating field technique[11] cannot remedy it. Finally, the range of $h\nu$ available between the photoelectric threshold and the optical absorption edge is rather small for convenient work on this effect.

5. CONCLUDING REMARKS

The salient result presented above is the abrupt rise in the photoelectric yield from BaO when $h\nu$ reaches 5 ev. A simple interpretation attributes this effect to emission from an occupied band of electron energy

---

[12] Malcolm Hebb, private communication (to be published); Phys. Rev. **81**, 702 (1951).

states with an upper edge 5 ev below the vacuum level. Energy distribution data are consistent with this picture. Krumhansl has arrived at a more complete energy structure by combining this result with the optical data obtained at Cornell.[13]

Photoelectric data for $h\nu<5$ ev are treated only

[13] J. Krumhansl, Phys. Rev. **82**, 575 (1951) (T). Calculations by D. A. Wright, Proc. Phys. Soc. (London) **60**, 13 (1948), place the edge and center of the occupied band 2.6 and 6.6 ev, respectively, below the vacuum level. This location of the band center is consistent with our result; the empirical value of the band width used by Wright in locating the edge was probably too large.

briefly. They are not believed to represent intrinsic emission from BaO. Yields in this region are variable and are ascribed to imperfections, some of which may be metastable; a more complete interpretation has not been attempted. Such yields are complicated further by Franck-Condon effects, by rapid changes in optical properties, and by an effect like the exciton-enhanced photoelectric emission observed in alkali halides.

Statistical Theory of Properties of Solid Solutions

R. SMOLUCHOWSKI

Carnegie Institute of Technology, Pittsburgh, Pennsylvania

Properties of binary solid solutions are considered from the point of view of the fluctuation of local composition in the crystalline lattice. These variations influence the properties of the alloys by varying the corresponding local concentration of electrons. A simple general statistical method is given for calculating properties of random and ordered solid solutions. The theory is applied to saturation magnetization, temperature coefficient of electrical resistivity, thermoelectric power, and to other properties in various alloys. A satisfactory agreement with experiment is obtained.

1. INTRODUCTION

THE studies of properties and of behavior of solid solutions are very important for understanding of metals. The change of composition makes possible, in favorable cases, the distinction between the influence of various factors and the estimate of the validity of the inevitable theoretical approximations. Many of the properties are closely related to the behavior of "free" electrons and in particular to their concentration. Typical examples here are saturation magnetization, magnetic susceptibility, electronic specific heat, Hall effect, electrical resistance, optical properties, etc. In the conventional theoretical approach to these phenomena, in accord with the band theory point of view, the metal is treated as a whole and the particular property is related to the average electronic concentration.

This strict band approach is justified when the electrons in question are very nearly free and their wavelength large compared to the atomic size. For more tightly bound electrons, as for instance in transition metals, the local electronic configuration of an atom and of its nearest surroundings should be taken into account. Such theories, if exact, are very complicated and therefore a simpler, approximate procedure is desired. The present paper describes such a method which incorporates the main features of the band theory and of the "local" point of view.

Since the average electronic concentration does not

depend upon the state of order in a crystal lattice, it is clear that a statistical treatment of local electronic configuration is particularly important in a consideration of the influence of order[1] on the properties and phenomena mentioned above. A first attempt in this direction was made[2] in a theory of the influence of order on magnetostriction of iron-cobalt alloys. It appeared later that the procedure there employed, although satisfactory for the specific purpose, led to a wrong dependence of the saturation magnetization on composition. The new method here presented is a simple general tool, it explains various experimental facts (including the relation between order and magnetostriction), and it applies to many alloy systems.

2. THE STATISTICAL METHOD

The basic procedure in the theory is to calculate first the fluctuations of the local electronic configuration, then to estimate their individual contributions to the particular property and finally to sum the contributions of the various fluctuations. The first question is thus the choice of the proper size n of the group of atoms within which the electronic fluctuation has a significant meaning for the particular property. A natural assumption is to consider as a basic unit an atom and its nearest neighborhood. In a close-packed lattice, either

[1] R. Smoluchowski, Intern. Conf. on Magnetism, Grenoble, 1950; J. phys. radium **12**, 389 (1951); Phys. Rev. **78**, 638 (1950).
[2] R. Smoluchowski and J. E. Goldman, Phys. Rev. **75**, 140 (1949).