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Structure in Optical Absorption of Barium Oxide Films*

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Measurements of the optical absorption of BaO films at temperatures between 15°K and 370°C are reported. Four absorption peaks between 3.8 ev and 4.5 ev are found for measurements at liquid nitrogen temperature or below. At least the two strongest peaks are thought to be caused by exciton absorption. The sharpness of the structure is found to depend upon substrate temperature during evaporation and upon the temperature at which the optical measurements are made.

MEASUREMENTS of the optical absorption of BaO films were made between 3500A and 2000A at temperatures between 15°K and 370°C. The films were evaporated and the absorption measurements made in a liquid helium cryostat similar to that described by Duerig and Mador.[1] The evaporating unit was mounted inside the bottom of the liquid nitrogen shield, and the fused quartz substrate was held by a copper or steel holder which was connected to the bottom of the liquid helium container. Two $\frac{1}{4}$-inch apertures in the substrate holder exposed the quartz; the BaO film being evaporated onto the lower, with the upper serving as a "blank." The platinum or platinum plus 10 percent rhodium evaporating filament was outgassed for two hours at 1450°C and then coated with Mallinckrodt "ultra-pure" barium carbonate in a minimum of nitrocellulose, amyl acetate binder. This was heated slowly in the vacuum system and converted to the oxide with the substrate in the "up" position. The substrate was then lowered into the evaporating position and the BaO film evaporated at temperatures of 1225°C to 1300°C. The substrate was usually heated during the evaporation by a heater of the type used in receiving-type vacuum tubes. Liquid nitrogen was always kept in the cryostat liquid nitrogen container as a pump for water vapor when a BaO film was present. Under these conditions no change in transmittance, such as would occur by hydrolysis of the film, was observed though data from some films was taken over a period of several days.

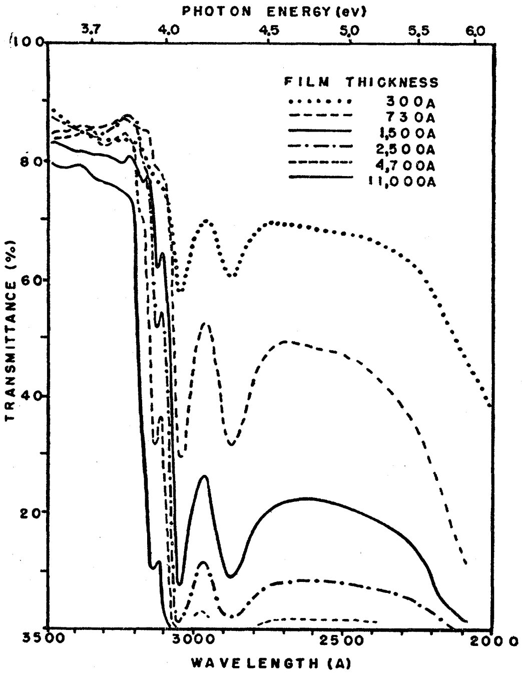

FIG. 1. Optical transmittance *vs* wavelength for BaO films of different thicknesses measured at −191±4°C. Fused quartz substrate at 370±10°C during evaporations.

The optical measurements were made using chopped light from a Nester Hydrogen arc, a 66-A/mm Bausch & Lomb grating monochromator, a 1P28 photomultiplier with a 33-cycle narrow-band amplifier and synchronous detector. A resolution of 6–8A was used and data were taken at intervals of 5 or 10A in the region of the observed structure.

When the optical transmittance was measured as a function of wavelength at liquid nitrogen temperature, much more structure was resolved than had been observed by Tyler[2] in the region near the absorption edge. This is shown in Fig. 1 for six BaO films of varying thickness. The relative thicknesses of these films were determined by time of evaporation and temperature of the evaporating filament using the data of Moore and Allison.[3] The absolute scale was selected by setting the absorption constant equal to 10^5 cm^{-1} at 2600A. This is the value obtained by Tyler, and weight measurements on some early films confirmed this magnitude of absorption constant. In addition to the strong absorption near 2000A, there also appear: (1) two strong absorption peaks at 2880A (4.30 ev) and 3050A (4.06 ev), (2) a small absorption peak at about 3140A (3.95 ev) on the edge of the 3050A absorption, and (3) a break in the slope of all of the curves for thicker

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[1] W. H. Duerig and I. L. Mador, Rev. Sci. Instr. **23**, 421 (1952).

[2] W. W. Tyler, Phys. Rev. **76**, 1887 (1949). The general features of Tyler's work agree with those reported here. The observation of more detail here was the result of greater resolution attainable with the above system and further refinements such as heating the substrate during evaporation of the BaO and a lower measurement temperature.

[3] G. E. Moore and H. W. Allison, Phys. Rev. **77**, 246 (1950).

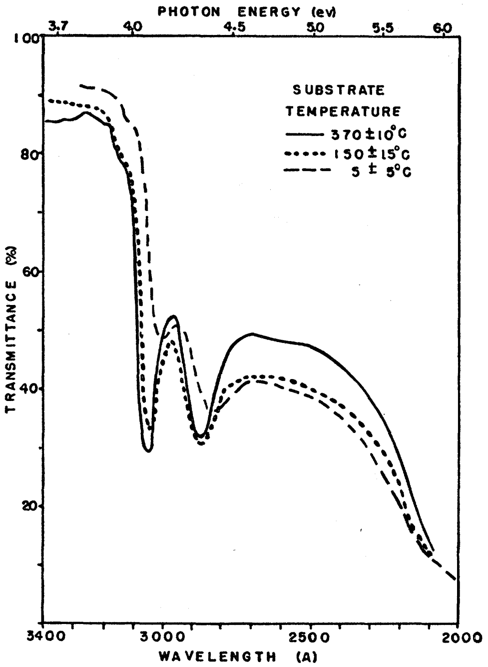

FIG. 2. Optical transmittance *vs* wavelength for different BaO films measured at −191±4°C showing the effect of substrate temperature during the evaporation.

films at about 3200A (3.88 ev) suggesting the presence of an unresolved peak. The "wiggles" and overlapping of the curves for wavelengths greater than 3200A are probably caused by interference phenomena and in part by experimental error. Scattering is probably responsible for the reduction in transmittance in this region.

As shown in Fig. 2, the positions of the transmittance minima were observed to shift, and the relative transmittance at the two major peaks to change, as a function of the temperature of the fused quartz substrate during the evaporation of the BaO film. This is presumably associated with a change in crystal perfection in the films. Such a dependence of film perfection on substrate temperature has also been observed by Russell and Eisenstein[4] for evaporated BaO films on nickel substrates. There is some indication that raising the evaporating filament temperature tends to sharpen the structure. However, this may be through the mechanism of heating the substrate.

The optical absorption constant *vs* wavelength is plotted in Fig. 3 for three measurement temperatures. The liquid nitrogen temperature curve was determined by plotting the logarithm of the transmittance *vs* film thickness for each wavelength and determining the absorption constant by the slope of the best straight line through these points. For the other measurement temperatures, the curves were determined by assuming that all of the loss in transmittance was caused by absorption. From the experience with the liquid nitrogen temperature data it was found that little error would result from this treatment for sufficiently thick films. Transmittance measurements at 15±5°K (using liquid helium as the coolant in the cryostat) showed structure only slightly sharper than at liquid nitrogen temperature. This presumably means that the sharpness of the absorption peaks at liquid nitrogen temperature is limited by zero-point lattice vibrations. It is possible, however, that lack of crystal perfection is responsible for a significant part of the observed width.

The two major absorption peaks are believed to be intrinsic to the BaO lattice. By use of Smakula's formula one calculates the concentration of absorption centers to be at least 1 percent and 0.5 percent for the peaks at 2880A and 3050A, respectively, after subtracting out a background "tail." Thus if this absorption were caused by defects or impurities, a very high concentration of these would be required. Defects associated with excess barium would perhaps be most likely. However, only about 0.04 percent excess barium is found in BaO single crystals colored by heating at 1120°C for 5 hours in a barium atmosphere.[5] In BaO films evaporated from platinum filaments, Moore and Allison[3] found less than 0.1 percent excess barium (their lower limit of detection). As a further experimental check on whether the structure could be associated with excess barium, a film was evaporated

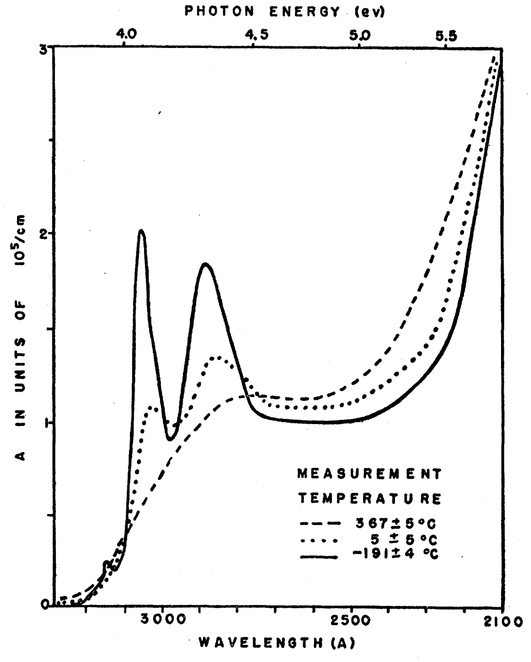

FIG. 3. Absorption constant (A) *vs* wavelength for BaO films measured at different temperatures. Fused quartz substrate at 365±15°C during evaporations.

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[4] P. N. Russell and A. S. Eisenstein, J. Appl. Phys. **25**, 954 (1954).

[5] Sproull, Bever, and Libowitz, Phys. Rev. **92**, 77 (1953).

from a filament consisting of a platinum plus 10 percent rhodium ribbon with a small tungsten ribbon spot-welded to it in a number of places. This arrangement was expected to give a film with the order of 10 percent excess barium.[6] The structure was not noticeably changed. An estimate of the minimum concentration of absorption centers associated with the peak at 3140A gives 0.03 percent while the value for the peak at 3200A would be considerably smaller.

The small widths of the major absorption peaks at half maximum (0.07 ev and 0.20 ev) and the fact that the structure sharpens with substrate temperature during evaporation of a film, appear to imply that the absorption is associated with the perfect lattice rather than with defects in the lattice. The sharpening of the structure at lower temperatures favors the view that these are exciton absorption peaks. Exciton absorption in BaO in the spectral region near 4.0 ev has been proposed to account for optical absorption and photoconductivity data,[7] photoemission,[8] and the temperature dependence of photoemission and photoconductivity.[9]

It should be noted that the absorption constant is at least as great as 300 cm^{-1} for single crystals of BaO prepared by a considerably different technique from these films,[5] and that the photoconductivity of these single crystals has a maximum in the region of the absorption peaks. Reflectivity measurements from single BaO crystals at low temperatures would be desirable to ascertain whether the density of these absorption centers is indeed as great in single crystals as it is in BaO films.

Overhauser[10] has pointed out that the observed structure can be understood in terms of an exciton model based on the tight binding approximation. The four absorption peaks arise from transitions between the ground state of the oxygen ion $(2p)^6$ and the four excited states of the $(2p)^5 3s$ configuration. The relative splittings of the four components can be fitted in terms of two constants: The exchange energy between $2p$ and $3s$ states and the spin-orbit splitting of the $(2p)^5$ ion core. A j-j coupling model is necessary. The absorption peaks at 3200A and 3140A are produced by transitions to excited states of angular momentum $J=0$ and 2, respectively. These peaks are weak because the transitions are forbidden by optical selection rules. The absorption peaks at 3050A and 2880A are produced by transitions to excited states for which $J=1$. They are allowed by optical selection rules and hence are strong.

The author is deeply indebted to Professor R. L. Sproull for his guidance and interest in this work and to Professors J. A. Krumhansl and A. W. Overhauser for discussions of interpretation.[11]

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[6] Based on private communication from G. E. Moore.

[7] W. W. Tyler and R. L. Sproull, Phys. Rev. 83, 548 (1951).

[8] Apker, Taft, and Dickey, Phys. Rev. 84, 508 (1951).

[9] H. B. DeVore and J. W. Dewdney, Phys. Rev. 83, 805 (1951).

[10] A. W. Overhauser (private communication).

[11] Since this work was performed, Mr. Koji Okumura has kindly communicated his studies of optical absorption of BaO films. He has found results similar to the 5°C curve of Fig. 3.

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Dynamics of Simple Lattices[*]

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The critical points (points where $\partial\omega/\partial x_i=0$ for all $i=1,2,3$) of the frequency ω of the lattice vibrations in wave number space (x_1,x_2,x_3), shown by Van Hove to exist for a very general class of crystals, are located for the monatomic simple, face-centered, and body-centered cubic lattices. The position and nature of the resulting singularities in the frequency distribution are found as a function of the ratio of force constants for second-nearest neighbors and nearest neighbors, and the qualitative features of the frequency distribution are thus determined. A method for using the information so obtained to determine the frequency distribution quantitatively is outlined.

I. INTRODUCTION

THE general problem we are concerned with is the finding of the energy eigenvalues of the Schrödinger equation for a system consisting of a very large number of coupled harmonic oscillators arranged in space in a simple lattice. Physically this system is interpreted as a crystal, the oscillators as the constituent atoms. Since the number N of atoms and hence the number of eigenvalues in a macroscopic crystal is of the order of Avogadro's number, an actual numerical evaluation of the latter is impractical even after an analytical expression for them has been obtained; and we are faced with the additional, usually more difficult, problem of finding the distribution function $g(E)dE$ of energy levels, defined as the density

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[*] Preliminary results reported at the Washington Meeting of the American Physical Society, April 1954 [Phys. Rev. 95, 617 (1954)].