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X-Ray Lattice Constant of Barium Oxide*

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Precision measurements of the x-ray lattice constant of pure BaO were made at temperatures between 8°K and 435°K with a back reflection symmetrical focussing camera. Room temperature measurements of colored BaO indicate a contraction of the lattice associated with the presence of excess barium.

I. EXPERIMENTAL PROCEDURES

THE low-temperature symmetrical focusing camera used for these measurements consisted of a liquid helium cryostat similar to that described by Duerig and Mador[1] with the lower end modified so as to contain the x-ray camera. The BaO powder specimen was held between two beryllium foil sheets clamped in a copper block and bolted to the lower end of the liquid helium container of the cryostat. An aperture in the liquid nitrogen shield permitted the x-ray beam to strike the specimen and the diffracted x-rays to return to the photographic film at room temperature.

The BaO samples were either polycrystalline specimens grown by the vapor deposition technique[2] or part of a compressed cylinder of BaO that had been held at about 1500°C for some hours in a vacuum as part of the crystal growing process (the presence of facets indicating some recrystallization takes place). These were ground in a mortar and passed through a sieve in a dry box desiccated with porous BaO and liquid nitrogen. Impurities were probably about 0.05% calcium, 0.02% strontium, 0.002% magnesium, and 0.001% molybdenum. The BaO powder was sprinkled onto one sheet of Be foil containing a couple of drops of ceresin wax[3] dissolved in benzene (dried with porous BaO), the second sheet of Be foil was placed on top and the "sandwich" clamped in the copper holder. The ceresin wax furnished adequate protection for the BaO from the atmospheric water vapor during the short periods required to mount the specimen in the cryostat and for changing the photographic films, even in the absence of the top sheet of beryllium foil. The cryostat was evacuated by a forepump during the exposures. A 0.003-in. copper-constantan thermocouple junction was imbedded with the BaO at the center of the "sandwich." Most specimens were not annealed after grinding because of the extreme instability of BaO in the presence of water vapor. However, one specimen was annealed by heating to 800°C in a quartz tube evacuated by a forepump and a liquid nitrogen trap. No change in the lattice constant was detected as a result of annealing.

Cobalt K_α radiation ($K_{\alpha 1}=1.78892$ A, $K_{\alpha 2}=1.79278$ A) was used and diffraction lines corresponding to $h^2+k^2+l^2$ equal to 36, 35, and 32 were obtained. Exposures were about 30 minutes at 25 kv and 15 ma. The films were calculated making use of Cohen's method[4] and gave an average standard deviation of about 0.0005 A. With the low-temperature camera the greatest source of error was due to the powder specimen being off the camera circumference and Cohen's correction appropriate for this error was employed. No correction for refractive index was made in view of the current disagreement as to whether one should be employed for powder diffraction patterns.

II. RESULTS FOR STOCHIOMETRIC BaO

Measurements on six films taken with the low-temperature camera gave a value of the lattice parameter of stochiometric BaO at 25°C of 5.53912±0.00013 A. This result was checked by six films taken with a commercial camera which yielded a result 5.53915 ±0.00013 A.

Measurements at other temperatures were made using liquid nitrogen, liquid helium, or dry ice and acetone as coolants or a heated oil bath in the cryostat liquid helium container. The results of measurements of four specimens at different temperatures are shown in Fig. 1. The liquid nitrogen and liquid helium measurements with one polycrystalline sample (open triangles) are evidently in error for some unknown reason (the three other liquid nitrogen measurements are in good agreement). The curve in the figure is that obtained by fitting the data with the equation[5]

$$\frac{a-a_{0^\circ\mathrm{K}}}{a}=\frac{\gamma}{3vK}U_T,$$

where γ is Grüneisen's number, K is the bulk modulus, v is the molar volume, and U_T is the thermal lattice energy less the zero-point energy. $a_{0^\circ\mathrm{K}}$ was estimated to be 5.5240 A and the constant of proportionality determined by using the lattice parameter value for 25°C. The curve shown in the figure results if the lattice energy is expressed as the sum of a Debye

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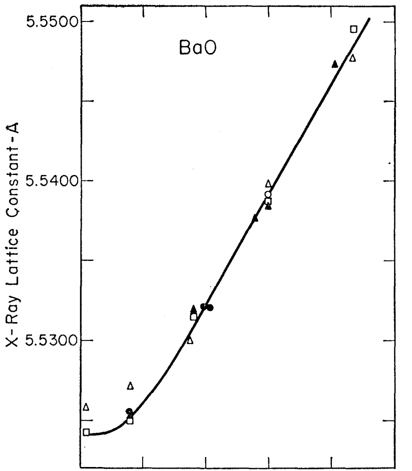

FIG. 1. X-ray lattice constant for several specimens of stochiometric BaO at various temperatures. Triangles represent two polycrystalline specimens grown by the vapor deposition technique, squares represent annealed sample, black dots are specimen from the heated compressed cylinder of BaO and open circle is the accurate room temperature value.

function with characteristic temperature of 173°K plus an Einstein function with characteristic temperature of 332°K (the function corresponding to that which Anderson[6] states best fits his BaO specific heat data), or if the lattice energy is expressed as a single Debye function with characteristic temperature of 280°K. The results are not sufficiently precise to distinguish between these functions though they lend support to Anderson's specific heat data by being consistent with it.

The linear expansion coefficient for BaO between 200°K and 400°K is found to be $12.8\pm0.9\times10^{-6}/°\mathrm{K}$. This value is somewhat smaller than the value $17.8\pm2.1\times10^{-6}/°\mathrm{K}$ reported by Eisenstein[3] between room temperature and 875°C.

III. COLORED BaO RESULTS

BaO crystals are colored by annealing in an atmosphere of barium (blue BaO).[7] X-ray lattice constant measurements were made at room temperature on two relatively lightly colored crystals prepared at this laboratory by Timmer and on two densely colored crystals used by Sproull, Bever, and Libowitz[8] (two films each were made with three of these specimens). The samples were prepared in the same way as the stochiometric BaO and were not annealed after grinding. Figure 2 shows the resultant x-ray lattice parameter *vs* the optically determined density of absorption centers, assuming an oscillator strength of $\frac{1}{2}$ and using Smakula's formula (chemical measurements yielded somewhat greater concentrations of excess barium). There is a considerable contraction of the lattice in the case of the densely colored crystals. If one were to assume a linear contraction of the lattice with percentage of excess barium, one would obtain the relation $\Delta a/a=-0.1$ (atomic percent excess Ba).

These results are consistent with the view that the blue coloration is associated with oxygen defects in the lattice in the form of F' centers.[8] A contraction of the lattice around the F' center might be expected because of the reduction in the repulsive interaction when the oxygen ion is replaced by the F' center. A contraction is observed, for instance, when a chloride ion replaces a bromide ion in KBr.[9] In addition, Burstein, Oberly, and Davisson[10] have concluded from measurements of the pressure dependence of color center absorption in alkali halides that there is a displacement of ions near an F center toward the vacant site.

BaO crystals grown from solution in molten barium are also colored (red BaO).[11] Chemical analysis by Libowitz indicated an excess barium by weight of about 0.1%. Kane[12] made optical absorption measurements of these crystals and found the density of absorption centers to be about 8×10^{18} cm^{-3} assuming an oscillator strength of $\frac{1}{2}$ and using Smakula's formula. Measurements of three specimens of the red BaO yielded values of the lattice parameter of 5.5351 ± 0.0007 A, 5.5337 ± 0.0010 A, and 5.5328 ± 0.0009 A at 25°C.

The lattice contraction observed with red BaO was smaller than that observed for an equivalent amount of excess barium in the blue crystals. The appearance of some contraction, however, implies that the red coloration is not caused by interstitial barium since interstitials would be expected to cause a considerable

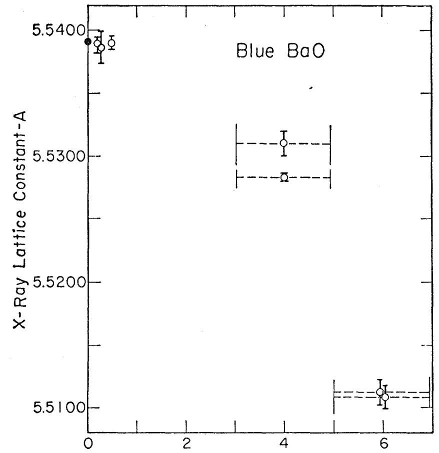

FIG. 2. The x-ray lattice constant of blue BaO *vs* the optically determined density of absorption centers.

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lattice expansion. The smaller lattice contraction may be caused by aggregation, perhaps in the form of colloids. The fact that there is any contraction at all points to one of two possibilities:

(1) F' centers in equilibrium with other defects; or

(2) less lattice strain associated with the centers responsible for the red absorption, as might be the case for defects intermediate in size between single oxygen vacancies and colloids.

In this connection, it should be emphasized that red BaO crystals are grown at about 900°C, while blue crystals are colored at about 1100°C.

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Classical Theory of Cyclotron Resonance for Holes in Ge

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Cyclotron resonance line shapes for holes have been calculated in the classical limit. The magnetic field was taken in the (001) direction. Because the cyclotron resonance frequency depends on the component of k parallel to the magnetic field (k_H), the line is shifted and broadened as compared to the simple theory with $k_H=0$. The shift of the maximum is about 3%, and the broadening (which is asymmetric) is about 40% for Ge, if $\omega\tau$ is taken as 7.5.

THE shape of cyclotron resonance absorption lines for Ge has been calculated treating the holes as classical particles. Quantum effects[1] become important at low temperatures and will be considered in a separate publication. It is easily shown that for a constant magnetic field H, the component of the quasi-momentum in the direction of H (k_H) is a constant of the motion. Thus for H in the (001) direction (the only case considered here), k_z is a constant. The equations of motion for k_x and k_y are then given by

$$\begin{aligned}\dot{k}_x&=\partial\mathcal{H}/\partial k_y\\ \dot{k}_y&=-\partial\mathcal{H}/\partial k_x,\end{aligned}\tag{1}$$

where for holes

$$\mathcal{H}=\frac{eH}{c}(\bar{A}k^2\pm[\bar{B}^2k^2+\bar{C}^2(k_x^2k_y^2+k_y^2k_z^2+k_z^2k_x^2)]^{\frac{1}{2}}).\tag{2}$$

The plus and minus refer to the light and heavy holes, respectively. The constants $\bar{A}$, $\bar{B}$, $\bar{C}$ are those reported by Dresselhaus, Kip, and Kittel[2] as A, B, C. One sees from Eq. (1) that k_x and k_y are canonically conjugate variables. The equations of motion for k_x and k_y will depend parametrically on k_z, and there will of course be a thermal distribution of k_z.

In order to estimate the effect of the thermal distribution of k_z a transport theory with a constant relaxation time τ was used. The theory is essentially that of Van Vleck and Weisskopf.[3] The formalism of the theory is similar to that used by Karplus and Schwinger.[4]

The calculations were performed starting with the following expression for the absorbed power per unit volume ρ:

$$\mathcal{P}=Ne\{\langle v_x(t)\rangle E_x(t)\}_{\text{Av}}\tag{3}$$

where E_x refers to an electric rf field in the [100] direction. N is the number of holes per unit volume and $v_x(t)$ is the velocity of a hole in the x direction. The brackets $\langle\,\rangle$ indicate an averaging over the time of collision and an averaging over the Boltzmann distribution. The braces refer to an average over time. Since k_x and k_y are canonically conjugate a new set of canonical coordinates P and Q, where $\mathcal{H}=P$, can be found. This leads to a considerable simplification. In terms of these new variables the averaging procedure gives

$$\mathcal{P}=\tfrac{1}{2}Ne^2E^2\tau\int_{-\infty}^{+\infty}dk_z\int_{P_0}^{\infty}dP\rho\beta\sum_{n=-\infty}^{+\infty}\frac{|v_x(n,P)|^2}{1+\tau^2(\omega+\omega_0n)^2}.\tag{4}$$

ρ is the Boltzmann factor

$$\rho=\frac{\exp\left(-\dfrac{\beta c}{eH}P\right)}{\Delta},$$

where

$$\Delta=\int_{-\infty}^{\infty}dk_z\int_{P_0}^{\infty}dP\int_0^{2\pi/\omega_0}dQ\exp\left(-\frac{\beta c}{eH}P\right),$$

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