

Wagner, Jr., *J. Phys. Chem. Solids* **26**, 233 (1965)], where native defect concentrations up to  $10^{19} \text{ cm}^{-3}$  are observed.

<sup>8</sup>See, J. Crank, *The Mathematics of Diffusion* (Oxford University Press, New York, 1964), Chap 8.

## ELECTRIC-FIELD MODULATION OF THE VIBRATIONAL ABSORPTION OF $\text{OH}^-$ IN $\text{KBr}$ †

Paul Handler and D. E. Aspnes

Departments of Physics and Electrical Engineering, and the Materials Research Laboratory, University of Illinois, Urbana, Illinois

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Most experimental measurements of the effects of the lattice on the  $\text{OH}^-$  impurity in alkali halides have been done at low temperatures. Kuhn and Lüty<sup>1</sup> have shown that the  $\text{OH}^-$  dipole is aligned along  $[100]$  directions in  $\text{KCl}$  at low temperatures; Feher, Shepherd, and Shore<sup>2</sup> and Bron and Dreyfus<sup>3</sup> have studied the paraelectric resonance of  $\text{OH}^-$ ; and Wedding and Klein have determined the depth of the wells in the  $[100]$  directions for several alkali-halide lattices by measuring the vibrational and librational modes of  $\text{OH}^-$ .<sup>4</sup> Except for optical-absorption and thermal-conductivity measurements at low temperatures for  $\text{OH}^-$  in  $\text{KCl}$  reported by Chau, Klein, and Wedding,<sup>5</sup> most of the data support the model of a dipole in an octahedral field first worked out by Devonshire.<sup>6</sup> We present further experimental evidence, based on electric-field modulation of the  $\text{OH}^-$  vibrational absorption line, that the Devonshire model does not fully explain the properties of  $\text{OH}^-$  in alkali-halide lattices at room temperature.

The experimental apparatus is similar to that used in many electroabsorption measurements.<sup>7</sup> A voltage at 1700 Hz was applied to the crystal and the variation in transmitted light intensity was phase-sensitively detected at twice the frequency. The electric field, of magnitude about a few times  $10^4 \text{ V/cm}$ , was normal to the incident radiation, and measurements were made with light polarized both parallel and perpendicular to the electric field as is shown in the inset of Fig. 1. Figure 1(a) shows the  $\text{OH}^-$  vibrational absorption near  $3610 \text{ cm}^{-1}$  at zero electric field. Figure 1(b) shows the change in absorption,  $\Delta\alpha$ , of the vibration line of the  $\text{OH}^-$  dipole in  $\text{KBr}$  with a  $[100]$  field orientation, for both parallel and perpendicular polarizations of the transmitted light. Figures 1(c) and 1(d) show similar results on  $\text{KBr}$  crystals with the electric field oriented in  $[110]$  and  $[111]$  directions. These samples were all cut from the same crystal, which had a doping of about

$540 \text{ ppm}$  of  $\text{OH}^-$ . Although not shown, qualitatively similar results were obtained for  $\text{KCl}:\text{KOH}$  for fields in the  $[100]$  direction. Figure 2 shows that the variation of the peak heights with field is quadratic.

Due to the small fractional changes in absorption ( $\sim 10^{-5}$ ) with electric field, the noise levels were high as indicated on the curves of changes in absorption. For this reason the line shapes are to be considered uncertain to this extent when quantitative comparisons are made. This leads to an uncertainty in the precise location of the peaks, as well as uncertainties in the ratio of the peak heights for parallel and perpendicular polarization for a given orientation. It is impossible to determine whether  $\Delta\alpha$  for perpendicular polarization changes sign in the wings as does  $\Delta\alpha$  for parallel polarization, although we believe that it does not. An additional error is introduced by the small depolarizing effect of the light scattering from the surface caused by its reaction with the atmosphere.

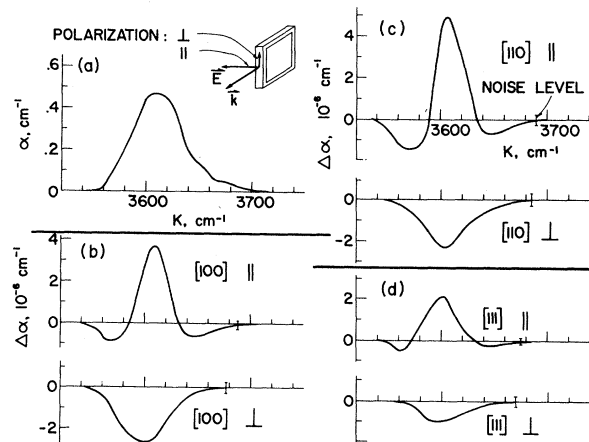


FIG. 1. The absorption and electric-field-induced change of absorption of the  $\text{OH}^-$  vibrational level in  $\text{KBr}$  for parallel and perpendicular polarizations of the incident light, for fields along  $[100]$ ,  $[110]$ , and  $[111]$  crystal directions.

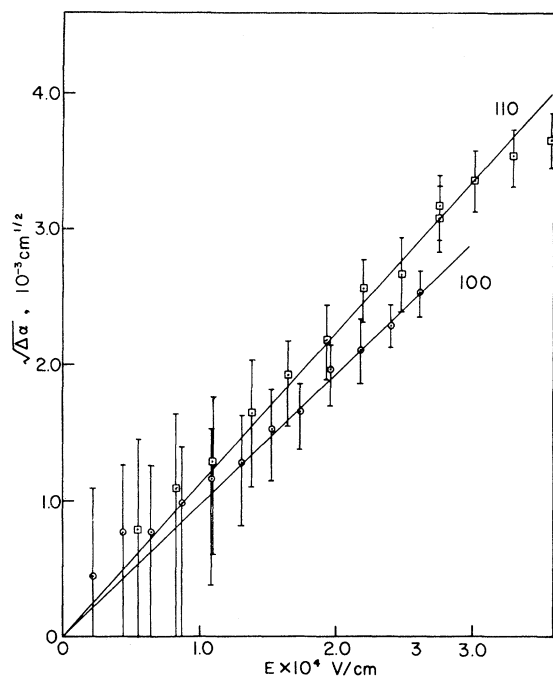


FIG. 2. The variation of the height of the parallel polarization peak of  $\text{OH}^-$  in KBr for [100] and [110] orientations of the electric field.

The following statements can be made for any orientation: (1) Parallel polarization shows line narrowing, increasing absorption at the center and decreasing absorption in the wings; (2) perpendicularly polarized curves show a decrease in absorption; and (3) both positive and negative peak heights vary quadratically with applied electric field. The gross behavior of the data suggests that at room temperature the  $\text{OH}^-$  dipoles behave as nonrotating dipoles with strong phonon coupling to the lattice. A shift of the line center is not observed. The change in absorption is then primarily a repopulation favoring orientation of the dipole along the field. For electric fields small compared with  $kT/p$ , where  $p$  is the magnitude of the dipole moment, this is a second-order effect. Since there are two directions transverse to the electric field, the polarization of light parallel to the applied field should yield a positive change in absorption equal to twice the negative change which occurs in perpendicular polarization. Observed ratios of the peak heights rather than areas yield the numbers  $1.4 \pm 0.3$ ,  $2.2 \pm 0.4$ , and  $2.1 \pm 0.7$  for the [100], [110], and [111] orientations, respectively.

The observed variation in the magnitude  $\Delta\alpha$

for different samples as seen in the figures is possibly caused by spatial variations in the doping of the single crystal from which the samples were cut. The ratio of parallel to perpendicular polarization absorption should be independent of these variations.

A model of six favored orientations for the dipole along the [100] axes will not explain the data. For [110] directions of the electric field, the perpendicular and parallel polarization curves should be identical for light propagated along a [100] direction. Moreover, for any value of the electric field there should be no change in absorption for either polarization if the field is oriented in the [111] direction. Neither of these results is observed, hence the simple model of six potential minima along [100] directions does not seem to apply at room temperature.

Use of second-order perturbation theory to calculate the effect of an electric field on the absorption of a Boltzmann distribution of freely rotating dipoles also fails to fit the experimental results. In this case, parallel polarization will yield roughly the experimental line shape for the change in absorption because the central peak arises from the admixture of  $j \pm 1, m_j$  states with the original  $j, m_j$  state with a corresponding second-order lifting of the forbidden  $j-j$  transition; renormalization of the wave function and repopulation favoring the less absorbing higher  $m_j$  values for a given  $j$  level combine to give the decreased absorption in the wings. For perpendicular polarization, theory gives an increase in absorption with the electric field, opposite to what is observed, because of the repopulation to the more highly absorbing (in perpendicular polarization) large  $m_j$  levels. We conclude that freely rotating  $\text{OH}^-$  dipoles do not exist in appreciable numbers at room temperature in KBr. This is reasonable in view of the 990°K well depth for  $\text{OH}^-$  in KBr.<sup>4</sup>

To explain the line narrowing observed in the parallel polarization requires knowledge of the process by which the absorption curve itself is broadened. Since the line is narrowed, the electric field must act to suppress the broadening through its interaction with the lattice. Consideration of this effect and others, all of which seem to be of second order, will probably explain the results of these experiments.

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## PRESSURE DEPENDENCE OF THE ORTHORHOMBIC-CUBIC TRANSFORMATION IN LEAD ZIRCONATE

Eliezer Rapoport

Chemical Physics Group of the National Physical and National Chemical Research Laboratories,  
South African Council for Scientific and Industrial Research, Pretoria, South Africa

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We have investigated the effect of pressure on the orthorhombic-cubic transformation in  $\text{PbZrO}_3$  by differential thermal analysis (DTA) in a piston-cylinder device. The technique has been previously described.<sup>1,2</sup>

Polycrystalline, sintered  $\text{PbZrO}_3$  samples<sup>3</sup> were placed in Teflon capsules.<sup>4</sup> A thin sheet of platinum separated the sample from a chromel-alumel thermocouple. In one experiment the sample was totally wrapped in platinum foil. Results of the various experiments were in excellent agreement with one another. Sharp and strong DTA signals were obtained on both heating and cooling, with a very slight temperature hysteresis ( $\sim 1^\circ\text{C}$ ) between heating and cooling at temperature change rates of  $\sim 2^\circ\text{C}/\text{sec}$ . The signal size gradually decreased with pressure until it became only vaguely detectable at around 20 kbar. On releasing pressure the signal size increased back to its original value. A second compression-decompression cycle exactly followed the behavior of the first one. The transition appears as a single transition on heating. However, it has been reported<sup>5</sup> that on cooling the transition appears to split into two, as revealed from the specific-heat curve measured on cooling. Recent dilatometric measurements<sup>3</sup> on pure lead zirconate also show the presence of a third phase, interpreted as ferroelectric.<sup>3</sup> This, however, is not confirmed by x-ray diffraction studies.<sup>6</sup> A ferroelectric phase also appears in  $\text{PbZrO}_3$  on application of a strong electric field<sup>7</sup> and is also known in the system  $\text{PbZrO}_3\text{-PbTiO}_3$ .<sup>8</sup>

Due to the negative volume change of the transition from the ferroelectric to the paraelectric phase,<sup>3</sup> the transition temperature should decrease with pressure. In the present study a search for this transition yielded several DTA signals at 142-146°C at atmospheric pressure in one experiment and at 167°C in another, as compared to 203°C reported by Sawaguchi, Shirane, and Takagi,<sup>5</sup> and 226-236°C reported by Tenney.<sup>3</sup> These signals became weaker and weaker upon repetition and were not obtained at higher pressures.

The phase diagram of  $\text{PbZrO}_3$  is shown in Fig. 1. The transition temperature increases linearly with pressure with an initial slope  $dT/dP$

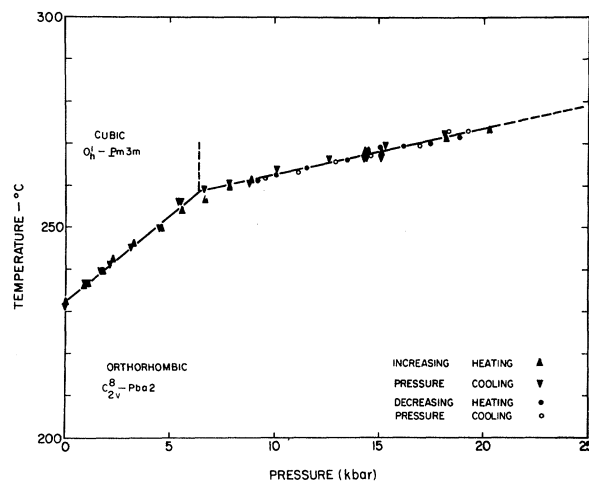


FIG. 1. Phase diagram of  $\text{PbZrO}_3$ .