

## Volume dependence of the electronic dielectric constant of crystals under hydrostatic pressure

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The analysis of the volume dependence of the electronic dielectric constant, recently performed by Sharma *et al.*, has been found to yield reasonable agreement with experimental data on the photoelastic effect for CuCl, CuBr, CuI, ZnO, ZnS, CdS, CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub> crystals. It has also been possible to understand the anomalous photoelastic behavior of rutile (TiO<sub>2</sub>).

A general theory concerning the dielectric constant of ionic crystals has been developed by Yamashita and Kurosawa<sup>1</sup> (hereafter referred to as YK) on the basis of the quantum-mechanical approach adopted earlier by Yamashita.<sup>2</sup> With the help of this theory, YK were able to explain the qualitative features of the photoelastic behavior of several alkali halides by studying the pressure dependence of the electronic dielectric constant or of the refractive index. More recently, Vedam and Schmidt<sup>3</sup> have discussed, at length, the utility of the YK dielectric theory to understand the photoelastic behavior of MgO crystal. In a recent paper Sharma *et al.*<sup>4</sup> have suggested a method within the framework of the YK theory for making a quantitative estimate of the strain derivatives of the electronic polarizabilities and the electronic dielectric constant. This method yields good agreement with experiment for alkali halides and MgO.

In the present addendum we intend to show that the photoelastic behavior of many other crystals can also be accounted for fairly well by deriving the strain dependence of the polarizability from the method of Sharma *et al.*<sup>4</sup> The details of the formulation are given in Ref. 4 and will not be repeated here except for the final expression which can be recast as

$$V\left(\frac{d\epsilon}{dV}\right) = -\frac{(\epsilon-1)(\epsilon+2)}{3}(1-\lambda), \quad (1)$$

where  $\epsilon$  is the electronic dielectric constant and  $V$  is the volume per ion pair. The strain-polarizability parameter  $\lambda$  is obtained as<sup>4</sup>

$$\lambda = -\frac{1}{3} \frac{R}{A_0 + A} \left(\frac{dA}{dR}\right) = \frac{R}{3\rho} \frac{(\alpha_f - \alpha)}{\alpha_f}, \quad (2)$$

where  $A_0$  and  $A$  are the interaction parameters.  $R$  is the interionic separation,  $\rho$  is the repulsive hardness parameter and can be taken<sup>5</sup> to be equal to 0.33 Å.  $\alpha_f$  and  $\alpha$  are, respectively, the free state and crystalline polarizabilities of the anions

listed in Table I. Values of  $R$  and  $\epsilon$  are given in Table II. Equation (2) has been derived by assuming that the variation of the polarizabilities of cations is negligible as compared to that of anions, to a first approximation.<sup>11,12</sup> Even in those crystals where the polarizabilities of cations are larger than those of anions, it has been found that the strain derivatives of the cation polarizabilities are much smaller than those for anions.<sup>11</sup>

If one assumes that the polarizabilities of ions do not change under compressive stress, then Eq. (1) is reduced to

$$V\left(\frac{d\epsilon}{dV}\right) = -\frac{(\epsilon-1)(\epsilon+2)}{3}. \quad (3)$$

It has been demonstrated by earlier investigators<sup>4,13,14</sup> that Eq. (3) yields large deviations from experimental data for alkali halides. It can be seen from Table II that the values of  $V(d\epsilon/dV)$  calculated from Eq. (3) are far from the experimental values. In some cases, viz., ZnO, ZnS, and CdS, even the sign of  $V(d\epsilon/dV)$  predicted on the basis of Eq. (3) is wrong. The situation can be remarkably improved if we take into account the strain dependence of the polarizability. It is very gratifying to observe from Table II that Eq. (1) predicts the correct sign and that the magnitudes of  $V(d\epsilon/dV)$  are closer to experimental values. Thus the consideration of the strain dependence of the polarizability is of crucial importance in the theory of photoelasticity. Values of the strain polarizability parameter  $\lambda$  corresponding to Eq. (2) are given in Table II. One can see

TABLE I. Electronic polarizabilities of ions (Å<sup>3</sup>).

| Ion          | F <sup>-</sup> | Cl <sup>-</sup> | Br <sup>-</sup> | I <sup>-</sup> | O <sup>2-</sup>   | S <sup>2-</sup>   |
|--------------|----------------|-----------------|-----------------|----------------|-------------------|-------------------|
| $\alpha_f^a$ | 1.04           | 3.66            | 4.77            | 7.10           | 3.92              | 10.3              |
| $\alpha^b$   | 0.87           | 2.96            | 4.10            | 6.24           | 1.69 <sup>c</sup> | 4.71 <sup>c</sup> |

<sup>a</sup> Reference 6.

<sup>b</sup> Reference 7.

<sup>c</sup> Reference 8.

TABLE II. Values of interionic separation  $R$  (Å), electronic dielectric constant  $\epsilon$ , strain polarizability parameter  $\lambda$ , and strain derivatives of the electronic dielectric constant  $V\left(\frac{d\epsilon}{dV}\right)$ .

| Crystal          | $R$  | $\epsilon$ | $\lambda$  |              | $V\left(\frac{d\epsilon}{dV}\right)$ |         | Experimental       |
|------------------|------|------------|------------|--------------|--------------------------------------|---------|--------------------|
|                  |      |            | Calculated | Experimental | Eq. (3)                              | Eq. (1) |                    |
| CuCl             | 2.35 | 3.7        | 0.45       | 0.44         | -5.13                                | -2.82   | -2.87 <sup>a</sup> |
| CuBr             | 2.46 | 4.4        | 0.35       | 0.57         | -7.25                                | -4.71   | -3.09 <sup>a</sup> |
| CuI              | 2.62 | 5.5        | 0.32       | 0.70         | -11.25                               | -7.65   | -3.36 <sup>a</sup> |
| ZnO              | 1.95 | 4.0        | 1.12       | 1.33         | -6.00                                | +0.72   | +1.97 <sup>b</sup> |
| ZnS              | 2.36 | 5.2        | 1.29       | 1.12         | -10.08                               | +2.97   | +1.18 <sup>b</sup> |
| CdS              | 2.52 | 5.2        | 1.38       | 1.42         | -10.08                               | +3.86   | +4.27 <sup>b</sup> |
| CaF <sub>2</sub> | 2.36 | 2.06       | 0.39       | 0.60         | -1.43                                | -0.88   | -0.58 <sup>c</sup> |
| SrF <sub>2</sub> | 2.51 | 2.07       | 0.41       | 0.41         | -1.45                                | -0.85   | -0.85 <sup>c</sup> |
| BaF <sub>2</sub> | 2.68 | 2.18       | 0.44       | 0.35         | -1.64                                | -0.92   | -1.07 <sup>c</sup> |

<sup>a</sup> Reference 15.

<sup>b</sup> Reference 9.

<sup>c</sup> Derived from the data on pressure dependence of refractive index cited by Andeen *et al.* (Ref. 10).

that  $V(d\epsilon/dV)$  is positive when  $\lambda$  is greater than one (for ZnO, ZnS, and CdS) and it is negative when  $\lambda$  is less than one. In fact, two effects are contributing to the variation of the electronic dielectric constant with volume. These are the change in density and the change in the polarizabilities of ions. If the first effect is dominant  $V(d\epsilon/dV)$  is negative, when the second effect overcompensates the first,  $V(d\epsilon/dV)$  becomes positive. It should be remarked that the cuprous halides are the only tetrahedrally coordinated binary crystals which have negative values of  $V(d\epsilon/dV)$ . This prediction is also corroborated by the recent photoelastic data published by Biegelsen *et al.*<sup>15</sup>

Finally, we discuss whether the present analysis can explain the anomalous photoelastic behavior of rutile (TiO<sub>2</sub>) crystal. This is an anisotropic material crystallizing in the tetragonal structure. The remarkably unusual behavior of this crystal has attracted the attention of numerous investigators.<sup>16-21</sup> The observed birefringence in TiO<sub>2</sub>, which is largest among all the solids of the same structure studied so far, can be accounted for only if one considers the anisotropy of the oxygen polarizability.<sup>18,20</sup> It was once suggested by Ruffa<sup>19</sup> that an isotropic model yields appropriate values of the electronic polarizabilities of ions in TiO<sub>2</sub> crystal. However, Ruffa's analysis has certain objectionable features<sup>21</sup> and, therefore, an

isotropic model can not account for the observed birefringence in rutile. This conclusion can, further, be supported by recent experimental and theoretical studies on photoelastic behavior of TiO<sub>2</sub> crystals.<sup>22,23</sup> The experimental data reveal a most interesting and distinct feature: The refractive index corresponding to the extraordinary ray decreases whereas that for the ordinary ray increases with pressure.<sup>22</sup> This implies that there are two strain polarizability parameters  $\lambda_1$  and  $\lambda_2$  for TiO<sub>2</sub>. These parameters can be evaluated theoretically employing the anisotropic model for the oxygen ion.<sup>18,20</sup> Accordingly one should assign two polarizabilities ( $\alpha_o^{\parallel}$  and  $\alpha_o^{\perp}$ ) to the oxygen ion, one parallel and one perpendicular to the plane of the titanium ions. Values of  $\alpha_o^{\parallel}$  and  $\alpha_o^{\perp}$ , as reported by Shanker and Verma,<sup>21</sup> are 2.23 and 1.39 Å<sup>3</sup>, respectively. In view of Eq. (2) we can write

$$\lambda_1 = (R/3\rho)(\alpha_f - \alpha_o^{\parallel})/\alpha_f \quad (4)$$

and

$$\lambda_2 = (R/3\rho)(\alpha_f - \alpha_o^{\perp})/\alpha_f \quad (5)$$

The values of  $\lambda_1$  and  $\lambda_2$  obtained from Eqs. (4) and (5) are 0.86 and 1.28, respectively, in good agreement with the corresponding experimental values (0.92 and 1.21) reported by Davis and Vedam.<sup>22</sup>

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- <sup>1</sup>J. Yamashita and T. Kurosawa, *J. Phys. Soc. Jpn.* **10**, 610 (1955).
- <sup>2</sup>J. Yamashita, *Progr. Theor. Phys.* **8**, 280 (1952).
- <sup>3</sup>K. Vedam and E. D. D. Schmidt, *Phys. Rev.* **146**, 548 (1966).
- <sup>4</sup>H. P. Sharma, Ram Niwas, Jai Shanker, and M. P. Verma, *Phys. Rev. B* **15**, 2363 (1977).
- <sup>5</sup>M. P. Tosi, *Solid State Phys.* **16**, 1 (1964).
- <sup>6</sup>L. Pauling, *Proc. R. Soc. A* **114**, 181 (1927).
- <sup>7</sup>J. Pirenne and E. Kartheuser, *Physica (Utr.)* **30**, 2005 (1964).
- <sup>8</sup>I. M. Boswarva, *Phys. Rev. B* **1**, 1698 (1970).
- <sup>9</sup>K. Vedam and T. A. Davis, *Phys. Rev.* **181**, 1196 (1969).
- <sup>10</sup>C. Andeen, D. Schuele, and J. Fontanella, *Phys. Rev. B* **6**, 591 (1972).
- <sup>11</sup>H. P. Sharma, Jai Shanker, and M. P. Verma, *J. Phys. Chem. Solids* **37**, 1077 (1976).
- <sup>12</sup>R. Srinivasan and K. Srinivasan, *J. Phys. Chem. Solids* **33**, 1079 (1972); *Phys. Status Solidi B* **57**, 757 (1973).
- <sup>13</sup>E. Burstein and P. L. Smith, *Phys. Rev.* **74**, 229 (1948).
- <sup>14</sup>K. G. Aggarwal and B. Szigeti, *J. Phys. C* **3**, 1097 (1970).
- <sup>15</sup>D. K. Biegelsen, J. C. Zesch, and C. Schwab, *Phys. Rev. B* **14**, 3578 (1976).
- <sup>16</sup>R. A. Parker, *Phys. Rev.* **124**, 1713 (1961).
- <sup>17</sup>F. E. Senftle, T. Pankey, and F. A. Grant, *Phys. Rev.* **120**, 820 (1960).
- <sup>18</sup>H. C. Bolton, W. Fawcett, and I. D. C. Gurney, *Proc. Phys. Soc. Lond.* **80**, 199 (1962).
- <sup>19</sup>A. R. Ruffa, *Phys. Rev.* **133**, 1418 (1964).
- <sup>20</sup>E. Uzan and V. Chandrasekharan, *J. Phys. (Paris)* **34**, 733 (1973).
- <sup>21</sup>Jai Shanker and M. P. Verma, *Phys. Rev. B* **12**, 3449 (1975).
- <sup>22</sup>T. A. Davis and K. Vedam, *J. Opt. Soc. Am.* **58**, 1416 (1968).
- <sup>23</sup>Jai Shanker, O. P. Sharma, and J. C. Sharma, *Solid State Commun.* **22**, 355 (1977).