

## Volume dependence of the electronic dielectric constant of ionic crystals

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The strain derivatives of the electronic dielectric constant of ionic crystals have been evaluated using the theory of dielectric constant proposed by Yamashita and Kurosawa. The calculated values for alkali halides and MgO agree reasonably well with the experimental values.

### I. INTRODUCTION

The volume dependence of the electronic dielectric constant  $\epsilon$  in ionic crystals has been a subject of theoretical as well as experimental investigations.<sup>1-4</sup> The strain derivative of  $\epsilon$  under hydrostatic pressure is directly related to the photoelastic constants which are experimentally measurable.<sup>5-13</sup> Thus an analysis of the variation of  $\epsilon$  with volume is useful for understanding the photoelastic behavior of solids. The experimental data on the temperature dependence of  $\epsilon$  can also be interpreted on the basis of volume dependence as suggested by Bosman and Havinga.<sup>2</sup> A remarkable feature of the experimental results is that the strain derivative of the electronic dielectric constant  $d\epsilon/dV$  has negative values for alkali halides whereas for MgO it has a positive value.

We have shown in earlier papers<sup>14,15</sup> that the observed photoelastic behavior of alkali halides and MgO can be adequately explained by taking into account the variation of polarizabilities  $\alpha$  with compression. In the present paper we suggest a method for evaluating the strain derivative of polarizabilities  $d\alpha/dV$  following the theory of dielectric constant formulated by Yamashita and Kurosawa.<sup>1</sup> In Sec. II we describe the method of calculation. Results obtained in the present paper have been presented and discussed in the light of experimental data in Sec. III.

### II. METHOD OF CALCULATION

Yamashita<sup>16</sup> proposed a quantum theory of dielectric constant and applied it to ionic crystals by assuming that the contribution of the positive ions to the electronic polarizability is much smaller as compared to that of the negative ions. He derived the polarizability of the negative ions from the perturbed wave function  $\phi(r)$  of the outermost  $p$  electrons expressed as

$$\phi(r) = \phi_0(r)(1 + \lambda r \cos\theta), \quad (2.1)$$

where  $\phi_0(r)$  represents the unperturbed wave function.  $\lambda$  is a variational parameter and  $\theta$  is measured from the field direction. Under the influence

of an electric field  $F$  at high frequencies so that the polarization due to ionic displacements is negligible, one can write for the energy change  $\Delta E$  per ion pair

$$\Delta E = -4\langle r^2 \rangle \lambda F - \frac{1}{2} \frac{4\pi}{3} \frac{(4\langle r^2 \rangle \lambda)^2}{2R^3} + A_0 \lambda^2 + A \lambda^2, \quad (2.2)$$

where  $R$  is the interionic separation. In Eq. (2.2) the first term represents the interaction energy between induced electric dipoles and the field, the second term arises from the mutual interaction of the induced electric dipoles, the third term is the change in the internal energy of a negative ion, where using the Kirkwood approximation, one can write  $A_0 = 3$  in atomic units, and the last term represents the mutual interaction of the deformed parts of the wave function  $\lambda \phi_0(r) r \cos\theta$ . One can define  $\langle r^2 \rangle$  as

$$\langle r^2 \rangle = \int r^2 \phi_0(r) d\tau. \quad (2.3)$$

The variational parameter  $\lambda$  can be determined from the extremum condition

$$\frac{\partial \Delta E}{\partial \lambda} = 0. \quad (2.4)$$

Equations (2.2) and (2.4) yield

$$\Delta E = - \frac{\frac{1}{2} (4\langle r^2 \rangle)^2 F^2}{[2(A_0 + A) - \frac{4}{3} \pi (4\langle r^2 \rangle)^2 / 2R^3]}. \quad (2.5)$$

The relation between  $\Delta E$  and  $\epsilon$  can be expressed with the help of the second-order Stark effect as follows<sup>17</sup>:

$$\Delta E = - (1/N) [(\epsilon - 1)/8\pi] F^2, \quad (2.6)$$

where  $N$  is the number of ion pairs per unit volume and for the NaCl structure can be put equal to  $1/2R^3$ . A comparison of (2.5) and (2.6) leads to the following relation

$$\epsilon - 1 = \frac{\pi/R^3}{a - \pi/3R^3} \quad (2.7)$$

with

$$a = \frac{A_0 + A}{(4\langle r^2 \rangle)^2}. \quad (2.8)$$

In view of the Clausius-Mossotti relation

$$(\epsilon - 1)/(\epsilon + 2) = \frac{4}{3}\pi\alpha/V. \quad (2.9)$$

Equation (2.7) yields

$$\alpha = 1/2a = (4\langle r^2 \rangle)^2/2(A_0 + A). \quad (2.10)$$

It is apparent from (2.10) that  $\alpha$  corresponds to the crystalline state as it depends upon interionic interaction  $A$ . The polarizability  $\alpha_f$  corresponding to the interaction-free state can be obtained by putting  $A = 0$  in (2.10). Thus we find

$$\alpha_f = (4\langle r^2 \rangle)^2/2A_0. \quad (2.11)$$

A comparison of (2.10) and (2.11) reveals that the polarizability of anions decreases in the crystalline state relative to the free state.

The strain derivative of  $\epsilon$  can be obtained by differentiating (2.7) with respect to  $R$ . Thus we find

$$\frac{R}{\epsilon} \frac{d\epsilon}{dR} = - \frac{(\epsilon - 1)(\epsilon + 2)}{\epsilon} \left( 1 + \frac{1}{3} \frac{R}{A_0 + A} \frac{dA}{dR} \right). \quad (2.12)$$

In order to evaluate the values of  $dA/dR$  one has to assume a simple functional dependence of  $A$  on  $R$ . The nature of  $A$  is very much similar to that of the repulsive potential in so far as  $A$  increases rapidly as the interionic separation decreases. Therefore,

one can assume for  $A$  the following simple form<sup>11</sup>:

$$A = Ue^{-R/\rho}, \quad (2.13)$$

where  $\rho$  can be identified as the Born repulsive hardness parameter.<sup>18</sup>

Insertion of (2.13) in (2.12) then leads to

$$\frac{R}{\epsilon} \frac{d\epsilon}{dR} = - \frac{(\epsilon - 1)(\epsilon + 2)}{\epsilon} \left( 1 - \frac{1}{3} \frac{A}{A_0 + A} \frac{R}{\rho} \right). \quad (2.14)$$

From Eqs. (2.10) and (2.11) we obtain

$$A/(A_0 + A) = (\alpha_f - \alpha)/\alpha_f. \quad (2.15)$$

Substituting for this quantity in Eq. (2.14) we find

$$\frac{R}{\epsilon} \frac{d\epsilon}{dR} = - \frac{(\epsilon - 1)(\epsilon + 2)}{\epsilon} \left( 1 - \frac{1}{3} \frac{R}{\rho} \frac{\alpha_f - \alpha}{\alpha_f} \right). \quad (2.16)$$

We have calculated  $(R/\epsilon)(d\epsilon/dR)$  from (2.16) for alkali halides and MgO using  $\epsilon$  from Lowndes and Martin,<sup>19</sup>  $R$  and  $\rho$  from Tosi,<sup>18</sup> free-ion polarizabilities from Pauling<sup>17</sup> and crystalline polarizabilities  $\alpha$  from Tessman, Kahn, and Shockley (TKS)<sup>20</sup> and from Perenne and Kartheuser (PK).<sup>21</sup>  $\alpha$  in MgO was taken from Boswarva.<sup>22</sup>

It should be mentioned here that Burstein and Smith<sup>5,6</sup> neglected the variation of polarizabilities under hydrostatic pressure and they used the relation

TABLE I. Values of  $(R/\epsilon)(d\epsilon/dR)$ .

Crystal	Calculated values		From Van Vechten's method	Experimental values	
	From (2.17)	From (2.16) a      b		$\frac{R}{\epsilon} \left( \frac{d\epsilon}{dR} \right)_T$	$\frac{R}{\epsilon} \left( \frac{d\epsilon}{dR} \right)_P$
LiF	-1.89	-0.18   -1.15	-1.24	-0.53, <sup>c</sup> -0.54 <sup>d</sup>	-0.62
LiCl	-3.02	-1.42   -1.66	-1.60		-1.39
LiBr	-3.53	-2.22   -2.47	-1.71		-1.33
LiI	-4.27	-3.22   -3.36	-1.81		-1.37
NaF	-1.59	-0.12   -0.96	-1.16		-0.73
NaCl	-2.47	-0.99   -1.21	-1.53	-0.97 <sup>c</sup>	-0.81
NaBr	-2.83	-1.72   -1.93	-1.64		-1.35
NaI	-3.35	-2.40   -2.53	-1.76		-1.43
KF	-1.77	+0.11   -0.96	-1.28		-0.55
KCl	-2.25	-0.88   -1.08	-1.49	-0.91, <sup>c</sup> -1.16 <sup>d</sup>	-1.00
KBr	-2.51	-1.43   -1.64	-1.59	-1.33, <sup>c</sup> -1.28 <sup>d</sup>	-0.99
KI	-2.90	-1.97   -2.09	-1.72	-1.45 <sup>c</sup>	-1.10
RbF	-1.89	+0.32   -0.94	-1.35		-0.46
RbCl	-2.26	-0.74   -0.96	-1.50		-0.93
RbBr	-2.49	-1.38   -1.59	-1.60		-1.69
RbI	-2.80	-1.82   -1.95	-1.69		-0.96
MgO	-3.39	+0.85	-1.48	+0.40, <sup>e</sup> +1.37, <sup>f</sup> +0.86 <sup>g</sup>	...

<sup>a</sup> Calculated using TKS polarizabilities in alkali halides.

<sup>b</sup> Calculated using PK polarizabilities in alkali halides.

<sup>c</sup> Reference 6.

<sup>d</sup> Reference 8.

<sup>e</sup> Reference 9.

<sup>f</sup> Reference 10.

<sup>g</sup> Reference 11.

$$\frac{R}{\epsilon} \frac{d\epsilon}{dR} = - \frac{(\epsilon - 1)(\epsilon + 2)}{\epsilon} \quad (2.17)$$

which is obtained from Eq. (2.16) if we neglect the second term inside the bracket on the right-hand side.

### III. RESULTS AND DISCUSSION

The values of  $(R/\epsilon)(d\epsilon/dR)$  calculated from (2.16) have been listed in Table I along with the experimental values. The experimental values of  $(R/\epsilon)(d\epsilon/dR)_T$  are derived from the measured photoelastic constants<sup>6-11</sup> and  $(R/\epsilon)(d\epsilon/dR)_P$  have been evaluated from the experimental data<sup>19,23</sup> on  $\epsilon$  at 2 and 290 K.

Values of  $(R/\epsilon)(d\epsilon/dR)$  for alkali halides are calculated using two different sets of crystalline polarizabilities, those due to TKS and PK in order to assess the sensitiveness of the results on polarizabilities. Both sets of polarizabilities yield  $(R/\epsilon)$

$(d\epsilon/dR)$  (Table I), in reasonable agreement with experimental data except in a few cases. The polarizabilities reported by TKS suggest positive values of  $(R/\epsilon)(d\epsilon/dR)$  for KF and RbF contrary to experimental data. PK have, however, remarked that the polarizabilities of lighter ions (e.g.,  $F^-$  ion) were poorly computed by TKS. It is very encouraging to note from Table I that  $(R/\epsilon)(d\epsilon/dR)$  calculated from the polarizabilities of PK are negative in KF and RbF.

Our values of  $(R/\epsilon)(d\epsilon/dR)$  are closer to experimental values than those calculated from the relation (2.17) derived by Burstein and Smith.<sup>5</sup> In the case of MgO, relation (2.17) yields a negative value of  $(R/\epsilon)(d\epsilon/dR)$  contrary to experimental data. In this respect (2.16) shows a remarkable improvement. Van Vechten<sup>24</sup> has recently developed a method for calculating  $(R/\epsilon)(d\epsilon/dR)$  based on dielectric dispersion theory. The values obtained by this method have also been included in Table I for the sake of comparison.

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