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Volume and Pressure: Dependence of Dielectric Constants

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Abstract – Studies on volume and pressure derivatives of dielectric constants of ionic crystals are useful to make a critical test of the theories of dielectric polarization and interionic forces operative in these crystals. Measurements of first, second and third order pressure derivatives of static or low frequency dielectric constant ε_0 have been performed for a number of ionic crystals. These experiments make use of these terminal geometric capacitance (TTGC) techniques. The details of experimental method based on TTGC measurements have been given by Lowndes and Martin. The TTGC method is better than the old immersion method mainly in two respects. First it is quicker method and secondly it does not use high dielectric constant liquids which can prove troublesome.

In fact the liquid-solid surface interactions change the dielectric constants by several percent. Among the various measurements based on TTGC the results obtained by Fontanella et alfor alkali halides may be considered to be most accurate. These investigators have assigned an uncertainty of only ± 0.2% for first derivatives of ε_0. On the other hand the uncertainties reported by other workers [20-26]are of the order of ± 5%.The results obtained by Fontanella et al have subsequently been corroborated by Bertels and Smith[40]. In fact the high accuracy achieved is due in part to the use of higher order terms to describe the variation of ε_0 with pressure and in part to the improved experimental techniques. Andeen et al have measured the pressure derivatives of $\varepsilon_0$of alkaline earth fluoride using the same experimental method.They report an uncertainty of ± 0.01% for the first order pressure derivatives of ε_0 for CaF_2,SrF_2 and BaF_2.Their results are in very good agreement with other investigations[40-54].The TTGC method has also been used to measure the temperature and pressure dependences of the dielectric constants of semiconductors.

- X -

The pressure derivatives of static dielectric constant are determined through the measurements of the pressure dependence of capacitance. The pressure derivatives can be reduced to volume derivatives using the relations given below

$$\frac{d\,\varepsilon_0}{d\,P} = \left\{ -\frac{V}{B_T}\left(\frac{d\,\varepsilon_0}{d\,V}\right)\right\} \qquad (4.1)$$

$$\frac{d^2\,\varepsilon_0}{d\,P^2} = -\frac{1}{B_T}\left(\frac{d\,\varepsilon_0}{d\,V}\right) + \frac{V}{B^2_T}\left(\frac{d\,\varepsilon_0}{d\,P}\right)\left(\frac{dB_T}{dV}\right) + \frac{V^2 d^2\,\varepsilon_0}{B^2_T}\left(\frac{}{d\,P^2}\right) \qquad (4.2)$$

And

$$\frac{d^3\varepsilon_0}{dP^3} = -\frac{1}{B_T}\left(\frac{d^2\varepsilon_0 2V}{dP^2}\right) - \frac{d\varepsilon_0 dB_T}{B^3_T dPdV}\left(\frac{V}{B^2_T}\right) + \frac{d^2\varepsilon_0 dB_T}{dP^2 dV}\left(\frac{}{B^3_T}\right)\left(\frac{V}{}\right) - \frac{d\varepsilon_0 d^2B_T}{dPdV^2}\left(\frac{}{}\right)\left(\frac{}{}\right)$$
$$\frac{2\,V^2}{B^4_T dP}\left(\frac{d\varepsilon_0}{dV}\right)\left(\frac{dB_T}{}\right) - \frac{2V^3 d^2\varepsilon_0}{B_T^3\;dV^2}\left(\frac{}{}\right) + \frac{2\,V^3}{B^4_T}\left(\frac{d^2\varepsilon_0}{dV^2}\right)\left(\frac{dB_T}{dV}\right) - \frac{V^3 d^3\varepsilon_0}{B_T^3}\left(\frac{}{dV^3}\right) \qquad (4.3)$$

Where $B_T = -V(dP/dV)$ is the isothermal bulk modulus. All the derivatives are taken at constant temperature. The experimental values of volume derivatives of ε_0 can be from equations (4.1) to (4.3) using measured data on the pressure derivatives of ε_0. Values of V ($d\varepsilon_0/dV$),V^2 ($d^2\varepsilon_0/dV^2$), and V^3 ($d^3\varepsilon_0/dV^3$) thus obtained from the experimental data.Values of volume derivatives of dielectric constant can also be calculated starting from the Claussius –Mossotti theory of dielectric constant and using interionic potentials. Such studies for alkali halides and other ionic crystals have been performed [56-60].A comparison of the calculated and experimental values of calculated and experimental values of the volume derivatives of ε_0 provides a rigorous test of various polarization and interionic potential models. On the basis of Claussius –Mossotti relation,i.e., using equations (2.6) and (2.10) we can write

$$V\left(\frac{d\,\varepsilon_0}{d\,V}\right) = \left(\frac{4\pi}{3}\,\frac{d\alpha_i}{dV} - \frac{4\pi\alpha_i 3V}{3V} + \frac{d\varepsilon_\infty}{(\varepsilon_\infty+2)^2}\,\frac{(\varepsilon_0+2)^2}{dV}\right)\frac{}{3} \qquad (4.5)$$

The first and second order volume derivatives of dielectric constants are then obtained from equation (4.4) as follows,

$$V^2\left(\frac{d^2\varepsilon_0}{dV^2}\right)=\left[\frac{4\pi}{3}\left(V\frac{d^2\alpha_i}{dV}\right)\frac{8\pi}{3}\left(\frac{d\alpha_i}{dV}\right)+\frac{8\pi}{3V}\alpha_i + \frac{6}{(\varepsilon_0+2)^2}V^2\left(\frac{d\varepsilon_0}{dV}\right)^2+\frac{3}{(\varepsilon_\infty+2)^2}\left(V^2\frac{d^2\varepsilon_\infty}{dV^2}\right) - \frac{6}{(\varepsilon_\infty+2)^3}V^2\left(\frac{d\varepsilon_\infty}{dV}\right)^2\right]\frac{(\varepsilon_0+2)^2}{3} \qquad (4.6)$$

The ion-displacement polarizability is given by

$$\alpha_i = [\ (Ze)^2/A] \qquad (4.7)$$

Where Ze is the magnitude of ionic charge and A is the force constant related to the short range –range potential energy ϕ(r) and its derivatives by the following expression,

$$A = [\phi^{II}(\ r) + (2/r)\ \phi^{I}(\ r)] \qquad (4.8)$$

Where the superscript I,II etc. represent the first and higher order derivatives with respect to r. The volume derivatives of α_i are obtained from equation (4.7) as follows (by assuming Z not to depend on volume)

$$\frac{d\alpha_i}{dV} = \frac{\alpha_i}{V}\left(-\frac{V}{A}\frac{dA}{dV}\right) \qquad (4.9)$$

And,

$$V\frac{d^2\alpha_i}{dV^2} = -\frac{\alpha_i}{V}\left(\frac{V^2}{A}\frac{d^2A}{dV^2} - 2\left(\frac{V}{A}\frac{dA}{dV}\right)^2\right) \qquad (4.10)$$

The volume derivatives of the short range force constant A can be obtained from equation (4.8) which yields

$$\frac{V}{A}\left(\frac{dA}{dV}\right) = \frac{r}{9A}\left[\phi^{III}(r) + (2/r)\phi^{II}(r) - (2/r^2)\ \phi^{I}(r)\ \right] \qquad (4.11)$$

and

$$\frac{V^2}{A^2}\left(\frac{d^2A}{dV^2}\right) = \frac{r^2}{27A}\left[\phi^{IV}(r) - (8/r^2)\phi^{II}(r) + (8/r^3)\ \phi^{I}(r)\right] \qquad (4.12)$$

It is clear from equations (4.5) and (4.6) in order that the volume derivatives of ε_∞ and α_i are required in order to evaluate the first and higher order derivatives of static dielectric constant. The method for evaluating the volume derivatives of ε_∞ and electronic Polarizabilities has been developed for NaCl type crystals as well as for CsCl type crystals. It should be mentioned that for ionic crystals. In general, the values of volume derivatives of ε_∞ are much smaller than the corresponding values of those of ε_0. This is mainly because the volume derivatives of ion –displacement Polarizabilities are much larger than those of electronic Polarizabilities.

Gibbs and Jarman [1962] have found empirically that the total Polarizability α_0 varies nearly as the square of the volume. This implies that

$$\frac{V}{\alpha_0}\left(\frac{d\alpha_0}{dV}\right) \simeq 2 \qquad (4.13)$$

Sharma et.al. (1977) have considered a more general relation of the form

$$\alpha_0 = KV^q \qquad (4.14)$$

Where K and q are constants for a given crystals. Using the experimental data on first and second order volume derivatives of constant ε_0 they have obtained values of q between 2 and 3 .The ion-displacement polarizability α_i and the short range force constant A also depend on the volume in a form similar to that represented by equation (4.14)as it is evident from the data on these quantities. In fact we note from equation (4.9) that $(V/\alpha_i)(d\alpha_i/dV)$ and (V/A)(dA/dV) are equal and of opposite sign to each other. It should be mentioned here that the importance of (V/A)(dA/dV) as a useful physical quantity for crystals has been established .Sherman has used this quantity to study the bond anharmonicities and pressure dependence of normal modes of vibrations, whereas Shankar and coworkers [ ]have made use of this to obtain some inter-relationships and thermodynamic quantities. There have been numerous attempts to investigate the volume dependence of e*/e .Taking the volume derivative of equation (2.23) we get,

$$\gamma_{TO} = -\frac{V}{\omega_{TO}}\left(\frac{d\omega_{TO}}{dV}\right) = \frac{1}{2}\left[\frac{V}{e^*}\frac{de^*}{dV} - \left(\frac{1}{(\varepsilon_\infty+2)} + \frac{1}{2(\varepsilon_0-\varepsilon_\infty)}\right)V\frac{d\varepsilon_\infty}{dV} + \left(\frac{1}{2(\varepsilon_0-\varepsilon_\infty)}\right)V\frac{d\varepsilon_\infty}{dV}\right] \qquad (4.15)$$

Where γ_{TO} is the transverse optic mode Gruneisen parameter. The exponential values of γ_{TO} for most of the alkali halides, silver halide and thallous halides have been reported by Lowndes and Rastogi [1976].It is thus possible to estimate (V/e^*) (de^*/dV) directly from experimental data using equation (4.15).An alternative method to evaluate the volume dependence of $e^*$is based on different polarization models such as the shell model exchange charge mode, deformation model and Phillips Lawaetz ionicity model (Jain and Shanker[124]).A comparison of the value of $(V/e^*)(de^*/dV)$ obtained from different models is presented in Table 4.3.The common feature of the results obtained from different models is that (V/e^*) (de^*/dV) is positive without any expectation.This implies that the decrease in the crystal volume due to the effect of pressure increases the overlap and distortion of ions, thereby causing the decrease in the Szigeti effective charge parameter (e^*/e).Values (V/e^*)(de^*/dV)obtained from the exchange charge model and the deformation dipole model are closer to each other and also with the experimental values Table(4.3).It has been pointed out that the features of the exchange charge model and the deformation dipole model are similar in certain respects and both the model take proper account of ionic overlap and distortions. This is the main reason for the detailed investigations of the dielectric properties of ionic crystals using these two models. It should also mentioned that the assumption that e^*/e does not change with volume,i.e (de^*/dV) =0, yields the values of γ_{TO} from equation (4.15) which are in reasonably good agreement with experimental data. On the other hand, some workers have found that (de^*/dV) is negative for all alkali crystals. Studies based on recent experimental data and correct formulation have revealed that (de^*/dV) should not be negative. It has been shown by Barron and Batana that the values of (de^*/dV) obtained by Jones were to be negative because he used a relation between short range force constant and compressibility which is valid only at atmospheric pressure. Barron and Batana have modified this relationship by considering the effect of applied pressure. The negative values of (de^*/d V) obtained by Vartosos[180] have been found invalid as he has used an incorrect relationship between the force constant and transverse optic mode frequency.The second order volume derivative of the effective charge parameter can also be calculated using the data on the volume derivatives of dielectric constants. Taking the volume derivative of equation (4.15) we get an expression for (d^2e^*/dV^2) in terms of the second order volume derivatives of ε_0,ε_∞ and ω_{TO}. The volume derivatives of $\omega_{TO}$and γ_{TO} can be evaluated with the help of the first Szigeti relation, which on differentiating yields,

$$\gamma_{TO} = -\frac{V}{\omega_{TO}}\left(\frac{d\omega_{TO}}{dV}\right) = -\frac{1}{2}\left(\frac{V}{A}\frac{dA}{dV} - \frac{V}{(\varepsilon_0+2)}\frac{d\varepsilon_0}{dV} + \frac{V}{(\varepsilon_\infty+2)}\frac{d\varepsilon_\infty}{dV}\right) \tag{4.16}$$

And on differentiating once more we obtain the volume derivative of the given function And on differentiating once more we obtain,

$$\frac{V}{\gamma_{TO}}\left(\frac{d\gamma_{TO}}{dV}\right) = 1 + \frac{V^2}{2\gamma_{TO}(\varepsilon_0+2)}\left[\frac{d^2\varepsilon_0}{d^2V} \quad \frac{V^2}{(\varepsilon_0+2)} - \frac{d^2\varepsilon_\infty}{d^2V} \quad \frac{V^2}{A^2} - \frac{d^2A}{d^2V} \quad \frac{V^2}{A^2} + \frac{dA}{dV}\left(\frac{}{}\right)^2\right.$$
$$\left. - \frac{V^2}{(\varepsilon_0+2)^2}\left(\frac{d\varepsilon_0}{dV}\right)^2 + \frac{V^2}{(\varepsilon_\infty+2)^2}\frac{d\varepsilon_\infty}{dV}\left(\frac{}{}\right)^2 \right] \tag{4.17}$$

Where the short range force constant A and its volume derivative are the same as given by the equations (4.8),(4.11) and (4.12).Values of γ_{TO} and its volume derivatives calculated from equations (4.16) and (4.17) have been found to present good agreement with experimental data.

It is possible to find some useful interrelationships between higher order elastic constants and pressure derivative of dielectric constants. Using the equation of state for the relationship between pressure and volume derivatives of the potential energy W, we can write

$$P = -\frac{dW}{dV} \tag{4.18}$$

The total potential energy W for an ionic crystal can be written as,

$$W = -(\alpha_M e^2/r) + \phi(r) \tag{4.19}$$

Where α_M is the Madelung constant and $\phi(r)$ is the short-range repulsive energy. Using equations (4.8),(4.18) and (4.19), we get

$$B_T = -V(dP/dV) = (A/3xr) + (4/3)P \tag{4.20}$$

$$\frac{dB_T}{dV} = \frac{A}{6xr^4}\left(\frac{V}{A}\frac{dA}{dV} - \frac{5}{3}\right) - \frac{16}{9}\frac{P}{V} \tag{4.21}$$

$$\frac{d^2B_T}{dV^2} = \frac{A}{12xr^7}\left(\frac{V^2}{A}\frac{d^2A}{dV^2} - \frac{2V}{A}\frac{dA}{dV} + 4\right) + \frac{112P}{27V^2} \tag{4.22}$$

Where x (=(V/r^3)) is a geometrical factor depending on the type of crystal structure. For NaCl –structure solids x=2.On solving equations (4.20 to 4.22) we get

$$A = -3xr(VP^I + 4P/3) \tag{4.23}$$

$$\frac{V}{A}\frac{dA}{dV} = \frac{3V^2P^{III} + 8VP^I + (4/3)P}{3VP^I + 4P} \tag{4.24}$$

$$\frac{V^2}{A^2}\frac{d^2A}{dV^2} = \frac{3V^3P^{III} + 12V^2P^{II} + 4VP^I - 8P/9}{3VP^I + 4P} \tag{4.25}$$

Where

$$P^I = (dP/dV), P^{II} = d^2P/dV^2, \text{ and } P^{III} = (d^3P/dV^3)$$

And these are directly related to the second, third, and fourth order elastic constants by the following expressions,

$$P^{I} = (C_{11} + 2C_{12})/3V \qquad (4.26)$$

$$P^{II} = \{[3(C_{11} + 2\,C_{12}) - (C_{111} + 6C_{112} + 2C_{123})]/9V^2\} \qquad (4.27)$$

$$P^{III} = [(C_{11} + 2C_{12}) + 3(C_{111} + 6C_{112} + 2C_{123}) + C_{1111} + 8\,C_{1112} + 6C_{1122} + 12\,C_{1123} - \frac{(C_{111} + 6C_{112} + 2C_{123})^2}{(C_{11} + 2C_{12})} + (C_{11} + 2C_{12})\left\{3 - \frac{(C_{111} + 6C_{112} + 2C_{123})}{(C_{11} + 2C_{12})}\right\} \left\{6 - \frac{(C_{111} + 6C_{112} + 2C_{123})}{(C_{11} + 2C_{12})}\right\} \qquad (4.28)$$

Thus equations (4.5) to (4.10) and equations (4.230 to (4.28) provide direct interrelations between the volume derivatives of dielectric constants and higher order elastic constants and higher order elastic constants. Using the data on second, third and fourth order elastic constants one can calculate A, (dA / dV) and d^2A/dV^2 with the help of equations (4.23) to (4.28). The volume derivatives of ε_0 and γ_{TO} are then estimated using equations (4.5) to (4.100,(4.16) and (4.17). The results thus reported have been found to present good agreement with experimental values. There are three components for the strain derivatives of each dielectric constant. They are represented by $W_{11,11}$ $W_{11,22}$ and $W_{12,12}$, defined as follows,(Shrinivasan [178]);

$$W^{0}{}_{ij,kl} = d\varepsilon^{0}{}_{ij} / d\eta_{kl} \qquad (4.29)$$

And

$$p^{\infty}{}_{ij,kl} = -W^{0}{}_{ij,kl} / \varepsilon^{2}{}_{\infty} \qquad (4.30)$$

Where the subscripts 0 and ∞ correspond to low frequency and high frequency dielectric constants respectively.$p^{\infty}{}_{ij,kl}$ are known as the photo-elastic or strain optical constants. In terms of quantities defined above the volume derivatives of the dielectric constants are

$$V \frac{d\varepsilon_\infty}{dV} = [-\,\varepsilon^{2}{}_{\infty}(p^{\infty}{}_{11,11} + p^{\infty}{}_{11,22})/3] \qquad (4.31)$$

$$V \frac{d\varepsilon_0}{dV} = [\,(w^{0}{}_{11,11} + 2w^{0}{}_{11,22})/3] \qquad (4.32)$$

The expressions $w_{ij,kl}$ and $p_{ij,kl}$ in terms of the shell model parameters have been obtained by Shrinivasan. Continuous efforts have been made to calculate these strain derivative components of dielectric constants.

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