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Study of Dielectric Constant & Polarizability

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Abstract – Within the framework of a classical model, an ionic crystal is regarded as composed of independently polarizable ions. The dielectric polarization in ionic solids is of two types (i) electronic and (ii) ionic. The polarization arising from the displacement of electron clouds of ions with respect to their nuclei is known as electronic polarization. In addition to this, the displacements of ions from their equilibrium configurations give rise to ionic Polarizability. Both these polarizations contribute to the dielectric constant at low frequencies i.e. in the infrared region. At high frequencies corresponding to the optical region the contribution of ionic displacement polarization becomes almost negligible due to large inertia of ions. The dielectric constant at such frequencies is known as electronic or optical dielectric constant ε∞ and arises entirely due to electronic polarization .The dielectric constant at low frequencies is known as static dielectric constant εo .It is one of the remarkable feature of ionic crystals that ε0 for these crystals differs appreciably from ε∞, values of εo is significantly larger than ε∞ .The relationship between ε∞ and electronic polarization is known as Lorentz-Lorenz (LL) relation. The relationship between static dielectric constant εoand corresponding Polarizabilities is known as the Claussius – Mossotti (CM) relation. The LL and CM relations along with the equation of motion for ions lead to the Szigeti relation [129]. The dielectric constants have also been related to the optical mode frequencies, viz. short-range Interionic forces [122-127].

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THE CLAUSSIUS-MOSSOTTI AND THE LORENTZ-LORENZ RELATIONS

To establish the relationship between the dielectric constant and polarizability, it is necessary to know the electric field effective in polarizing an atom or ion in a dielectric substance. It is a problem of central importance to find correctly the field, which acts on and polarizes an atom. This field is called Lorentz field. The effective field on an ionic site in cubic ionic crystals can be expressed as,

$$E_{eff} = E + \frac{4\pi P}{3} \qquad (2.1)$$

Where E is macroscopic electric field is applied externally dielectric polarization and 4π/3 is the Lorentz factor. The validity of above equation in solids has been discussed by several investigators [2-5,8]. Dielectric constant is connected with the polarization and field through the expression,

$$D = E + 4\pi P \qquad (2.2)$$

This displacement vector D and the electric field E are related through optical dielectric constant ε_∞ as,

$$D = \varepsilon_\infty E \qquad (2.3)$$

So that,

$$(\varepsilon_\infty - 1)\, E = 4\pi P \qquad (2.4)$$

The dielectric polarization P is related to the Polarizability as,

$$P = P_m / V_m = \alpha_m E_{eff} / V_m \quad (2.5)$$

Where P_m ,V_m and α_m are the dipole moment, volume and polarizability of one molecule respectively. From the above equations it follows that,

$$\frac{(\varepsilon_\infty - 1)}{(\varepsilon_\infty + 2)} = \frac{4\pi\alpha_m}{3\ Vm} \qquad (2.6)$$

In case of simple and ideally ionic crystal one can write

$$\alpha_m = \alpha_{(+)} + \alpha_{(-)} \qquad (2.7)$$

So that,

$$\frac{(\varepsilon_\infty - 1)}{(\varepsilon_\infty + 2)} = \frac{4\pi\alpha_\infty}{3\,Vm} \qquad (2.8)$$

In low frequency region the infraredpolarizability become significant in case of ionic crystals and thus equation (2.8) can be expressed as,

$$\frac{(\varepsilon_0 - 1)}{(\varepsilon_0 + 2)} = \frac{4\pi}{3\,Vm} (\alpha_+ + \alpha_- + \alpha_I) \qquad (2.9)$$

Where ε_0 is the low frequency dielectric constant and α_I is the infrared polarizability,

$$\alpha_I = \frac{Z^2 e^2}{A} \qquad (2.10)$$

Where A, the force constant between nearest neighbours Which can be shown to be related to the compressibility β and Interionic separation R_o as follows,

$$A = \frac{6R_o}{\beta} \qquad (2.11)$$

The form of equation (2.11) correspond to the ‘ NaCl’ structure.

SZIGETI RELATIONS

In ionic crystals there are two types of ions, positive ions and negative ions. The static ionic displacement is determine by the force constant ‘A’ as,

$$Au = ZeE \qquad (2.12)$$

Where u is the displacement of negative ions carrying a charge ‘Ze’ relative to a relative to a positive ion in the long wavelength limit.The ionic Polarizability is given by

$$P_{ion} = Nzeu = \frac{N(Ze)^2 E}{A} \qquad (2.13)$$

Where N is the number of ion pairs per unit volume and hence is equal to 1/V.

The CM and LL can be rearranged in the following form

$$\varepsilon_o = \frac{(1 + 2\phi + 2\theta/A)}{(1 - \phi - \theta/A)} \qquad (2.14)$$

and

$$\varepsilon_\infty = \frac{(1 + 2\phi)}{(1 - \phi)} \qquad (2.15)$$

Where

$$\phi = (4\pi/3V)\alpha_\infty \qquad (2.16)$$

and

$$\theta = (4\pi/3V)(Ze)^2 \qquad (2.17)$$

The transverse optic phonon frequency in the limit of long wavelength is determined by the equation of motion

$$\mu \frac{d^2u}{dt^2} + Au = ZeE = (4\pi/3)\,ZeP \qquad (2.18)$$

Where μ is the reduced mass per ion pair .The total Polarization P is now given by

$$P = P_e + P_i = N(\alpha_+ + \alpha_-)\,4\pi P/3 + NZeu \qquad (2.19)$$

If $u = u_o \exp(-i\omega_{To}t)$,then we have,

$$\mu\omega^2_{To} = \{A - (\theta/1-\phi)\} = \left[A - \frac{(4\pi/3)\,N(Ze)^2}{(4\pi/3)N(\alpha_+ + \alpha_-)} \right] \qquad (2.20)$$

Now if we eliminate θ between equations with help of equations (2.14),(2.15 and (2.20),we get the following relations,

$$\mu\omega^2_{To} = \frac{(\omega_0+2)}{(\omega_\infty+2)} = A = 6R_0/\beta \qquad (2.21)$$

and

$$(\varepsilon_0 - \varepsilon_\infty) = \frac{4\pi N \quad (\varepsilon_\infty+2)^2 (Ze)^2}{9\mu\omega^2_{To}} \qquad (2.22)$$

Equation (2.21) and (2.22) are known as the first and second Szigeti relations respectively [1]. The first Szigeti relation connects the compressibility β with other observed quantities whereas the second Szigeti relation connects the dielectric constants and transverse optic mode frequency of optical vibration. These two relations have been widely used to discuss the theories of dielectric constant and compressibility of binary crystals. In fact the Szigeti relations are not satisfied with experimentally observed quantities and therefore, the concept of effective compressibility and effective ionic charge have been introduced. The introduction of such concept yields the following relations,

$$\beta^* = \frac{6R_0}{\mu\omega^2_{To}} \left[\frac{(\omega_\infty+2)}{(\omega_0+2)} \right] \qquad (2.23)$$

and

$$(\varepsilon_0 - \varepsilon_\infty) = \frac{(\omega_0+2)^2}{9} \, \frac{4\pi N}{\mu\omega^2_{To}} (Z^* e)^2 \qquad (2.24)$$

Values of Szigeti effective charge parameter (e^*/e) calculated from equation (2.24) are found to be substantially lower than its normal value 1. These range between 0.7 and 0.8 for most of the alkali aldihides studied by Lowndes and Martin [105]. The values of (e^*/e) are much lower for less ionic crystals [115]. The deviations of ($e*/e$) as well as β from their normal values indicate the failure of (e^*/e) of classical theory of dielectric behaviour of crystals. The basic assumptions on which the Szigeti relations are based are as follows,

(i) The effective field is given by $E_{eff} = E + 4\pi P/3$.

(ii) The ions are not distorted. They are considered to be spherical and polarizable.

(iii) The short range interactions are considered to be operative only between nearest neighbour and three body interactions are neglected.

It has been shown that second neighbour and three body interactions play important role in modifying the first Szigeti relation given by equation (2.24) for the effective charge parameter is concerned with ionic distortions. The distortion dipole moment arising from the deformation of ions is mainly responsible for deviating ionic charges.

MOTT LITTLETON POLARIZATION MODEL

The Claussius –Mossotti between dielectric constant and Polarizability is based on the assumption that effective polarization field at ion sites is given by equation (2.1).It has been demonstrated that equation(2.1) does not remain valid when ions overlap appreciably with each other .As it well known that ions overlap, the validity of equation (2.1) is doubtful. The effect of over all of ions has been considered phenomenological by Mott and Gurney [3] and according to them one should divide the total polarization 'P' in to three parts,

$$P = P_1 + P_2 + P_x \qquad (2.25)$$

Where $P_1$and P_2 represent the electronic polarization of cations and anions, respectably.P_x is the polarization due to relative displacement of ions. The fields due to relative displacement of ions. The fields effective in polarizing the cations, anions and displacing the ions from their original positions are, respectably given by the following equations,

$$(E_{eff})_1 = E + (4\pi/3)[P_1 + (P_2 + P_x)\delta] \qquad (2.26)$$

$$(4\pi/3)[P_2 + (P_3 + P_x)\delta] \qquad (2.27)$$

$$(E_{eff})_2 = E +$$

$$(E_{eff})_3 = E + (4\pi/3)[P_3 + (P_1 + P_x)\delta] \qquad (2.28)$$

whereδ is a parameter representing the extent of overlap between ions. $\delta=1$ correspond to no overlap ions and leads to normal CM relation. If we define the Polarizabilitiesα_1, α_2,α_3 and α_x corresponding to P_1,P_2, and P_x, then,

$$P_1 = \alpha_1 / V \left\{ E + (4\pi/3)[P_1 + (P_2 + P_x)\delta] \right\} \qquad (2.29)$$

The static or low frequency dielectric constant ε_0 in ionic crystal is defined as,

$$P_1 = \alpha_1 / V \left\{ E + (4\pi/3)[P_1 + (P_2 + P_x)\delta] \right\} \qquad (2.29)$$

$$P_2 = \alpha_2 / V \left\{ E + (4\pi/3)[P_2 + (P_3 + P_x)\delta] \right\} \qquad (2.30)$$

$$P_3 = \alpha_3 / V \left\{ E + (4\pi/3)[P_2 + (P_1 + P_x)\delta] \right\} \qquad (2.31)$$

After solving equations (2.29),(2.30)and(2.31)we obtained the following expressions,

$$\frac{(\varepsilon_0 - 1)}{4\pi} = \frac{(P_1 + P_2 + P_x)}{E} \qquad (2.32)$$

Where

$$P_1 / E = 1/\Delta\{ N\alpha_1 + (4\pi/3)N^2(\delta-1)[\alpha_1\alpha_2 + \alpha_x\alpha_1] + (4\pi/3N)^2 N \alpha_1\alpha_2\alpha_x (\delta-1)^2 \} \qquad (2.33)$$

$$P_1 / E = 1/\Delta\{ N\alpha_1 + (4\pi/3)N^2(\delta-1)[\alpha_1\alpha_2 + \alpha_x\alpha_1] + (4\pi/3N)^2 N \alpha_1\alpha_2\alpha_x (\delta-1)^2 \} \qquad (2.33)$$

$$P_2 / E = 1/\Delta\{ N\alpha_2 + (4\pi/3)N^2(\delta-1) [\alpha_1\alpha_2 + \alpha_x\alpha_2] + (4\pi/3N)^2 N \alpha_1\alpha_2\alpha_x (\delta-1)^2 \} \qquad (2.34)$$

$$P_x / E = 1/\Delta\{ N\alpha_x + (4\pi/3)N^2(\delta-1) [\alpha_x\alpha_2 + \alpha_x\alpha_1] + (4\pi/3N)^2 N \alpha_1\alpha_2\alpha_x (\delta-1)^2 \} \qquad (2.35)$$

$$\begin{aligned} \Delta = [1 - (4\pi/3)N(\alpha_1 + \alpha_2 + \alpha_x) + \{(4\pi/3)N\}^2(\alpha_1\alpha_2 + \alpha_2\alpha_x + \alpha_1\alpha_x)(1-\delta)^2 \\ \{(4\pi/3)N\}^3(\alpha_1\alpha_2\alpha_x)(1 - 3\delta^2 + 2\delta^3)] \end{aligned} \qquad (2.36)$$

The following expression for dielectric constants are obtained corresponding to $\delta=0$

$$\frac{(\varepsilon_\infty - 1)}{4\pi} = \frac{\alpha_1/V}{\left[1 - (4\pi/3)\,\alpha_1/V\right]} + \frac{\alpha_2/V}{\left[1 - (4\pi/3)\,\alpha_2/V\right]} \qquad (2.37)$$

and

$$(\varepsilon_0 - \varepsilon_\infty) = \frac{4\pi(\alpha_x/V)}{1 - 4\pi(\alpha_x/V)} \qquad (2.38)$$

or,

$$\frac{(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 - \varepsilon_\infty + 3)} = \frac{4\pi}{3}\left[\alpha_x/V\right] \qquad (2.39)$$

For δ=1,we get the following expression for ε_0 and ε_∞ (Lorentz- Lorenz and CM relations),

$$\frac{(\varepsilon_\infty - 1)}{(\varepsilon_\infty + 2)} = \frac{4\pi\left[\dfrac{\alpha_1+\alpha_2}{V}\right]}{3} \qquad (2.40)$$

$$\frac{(\varepsilon_0 - 1)}{(\varepsilon_0 + 2)} - \frac{(\varepsilon_\infty - 1)}{(\varepsilon_\infty + 2)} = \frac{4\pi}{3}\left[\frac{\alpha_x}{V}\right] \qquad (2.41)$$

Equation (2.37) and (2.39) were first derived by Mott and Littleton [111] taking δ =0. An attempt has been made by Shanker and Sundraj [158] to obtain the dielectric constants for intermediate values of δ between o and 1.

The effect of introducing δ in the effective polarization fields has also been investigated on the transverse optic mode frequency ω_{To}. Mott and Gurney have derived the following expression [111].

$$\frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + 1/3\,\delta(\varepsilon_\infty - 1)]^2} = \frac{4\pi(Ze)^2}{V\mu\omega^2_{To}} \qquad (2.42)$$

Where V and μ are the volume and reduced mass per ion pairs respectively. Ze is magnitude of ionic charge. Putting δ =1,in the equation (2.42) yield,

$$\frac{(\varepsilon_0 - \varepsilon_\infty)}{(\varepsilon_0 + 2)^2} = \frac{4\pi(Ze)^2}{V\mu\omega^2_{To}} \qquad (2.43)$$

Which is the **Szigeti relation** .For δ =0, the equation (2.42) reduces to,

$$(\varepsilon_0 - \varepsilon_\infty) = \frac{4\pi(Ze)^2}{V\mu\omega^2_{To}} \qquad (2.44)$$

This equation was first derived by Born [77-79] and subsequently used by Lucovsky et al[116] to discuss the nature of localized and non-localized effective charges.

LOCALIZED EFFECTIVE CHARGE MODEL

The concept of localized charge parameter was introduced by Burstein [81], which has been widely used to discuss the nature of chemical bond and dielectric properties of alkali halide crystals [2,6-15]. In these crystals the oscillator strength of the transverse optic mode phonons is reflected in the difference in the squares of the longitudinal optic (LO) and transverse optic phonon frequencies, or in terms of difference between low frequency dielectric constant ε_0 and high frequency dielectric constant ε_∞. In fact the optic mode frequencies are related to the dielectric constants by Lyddane-sachs-Teller (LST) relationship,

$$\frac{\omega^2_{Lo}}{\omega^2_{To}} = \frac{\varepsilon_o}{\varepsilon_\infty} \qquad (2.45)$$

The oscillator strength of the transverse oscillator (TO) phonon is commonly described by either of two effective charge parameters e^*_T the macroscopic or transverse, or e^*_S the Szigeti effective charge. Of these charges, e^*_T is independent of the model and is calculated from readily observable quantities. On the other hand e^*_S is model dependent, in particular, requiring assumptions on the form of effective field. In fact e^*_T is a measure of the linear electric moment per unit cell and includes contributions from charge localized near the ion sites as well as charge distributed throughout the unit cell. Thus we can write,

$$e^*_T = e^*_l + e^*_{nl} \qquad (2.46)$$

Where$^*_{nl}$ is the non-localized charge. The effective localized charge e^*_l is assigned to be on the ion sites. The magnitudes of e^*_l is derived from the dipole interaction frequency.

To develop a phenomenological model for calculating the localized effective charge parameter, it is considered that there are two contributions to the transverse optic mode frequency ω_{To}. One of these is a mechanical or spring constant frequency derived from dipole-dipole interaction. The one can write,

$$\omega^2_{To} = \omega^2_o \Omega^2_{DD} \qquad (2.47)$$

Where ω_0 is the mechanical frequency and Ω_{DD} is the dipole interaction frequency. The localized effective charge parameter e^*_l is derived from the relation,

$$= \quad \Omega^2_{DD}\omega^2_{o}\omega^2_{T\bar{o}}- \qquad (2.48)$$

$$= \left[\frac{4\pi e^2}{3\mu V}\right] e_l^{*2} \qquad (2.49)$$

The factor (1/3) on the right of equation (2.48) reflects the cubic symmetry. In deriving equation (2.48), it has been assumed that there is no field correction. Although this assumption may be nearly true for covalently coordinated structures, but for highly ionic solids it is necessary to take full account of local field correction[10,11].When the local field correction is taken in to account, equation (2.48) is modified as,

$$e_l^{*2} = \frac{3\mu V}{4\pi e^2}\left[(\omega^2_{o}\varpi^2_{To})\right]\frac{(3)^2}{(\varepsilon_\infty + 2)^2} \qquad (2.50)$$

The effect of screening of the macroscopic field by the inter band electronic transition can be considered rigorously by writing

$$\frac{e_l^{*2}}{\varepsilon_\infty} - \frac{3\mu V}{4\pi e^2}\left[(\omega^2_{o}\text{-}\omega^2_{To})\right]\frac{(3)^2}{(\varepsilon_\infty + 2)^2} \qquad (2.51)$$

Equation (2.50) considers, the screening as well as local field correction (2.48 to 2.50) that calculation of e^*_l requires the evaluation of Ω^2_{DD}orω^2_o. For calculating the mechanical frequency ω_o one has to adopt interionic potential model, which leads to an expression for ω_o in terms of elastic constants.

If one assumes that there are only central nearest short range forces acting on the effective ion cores, then it may be shown that,

$$\omega^2_o = (\,3Ve^2/r^6_0\,\mu)B^* \qquad (2.52)$$

Where B^* is the reduced bulk modulus,

$$B^* = 1/3\,(\,C^*_{11} + 2C^*_{12}) \qquad (2.53)$$

If one considered the three body interaction within the framework of the model developed by Lundqvist [12]then the following expression is obtained,

$$\omega^2_o = 12\,(\,Ne^2/\mu)\{\,B^* + C^*_4 - C^*_{12}) \qquad (2.54)$$

This equation (2.54) takes into account the deviations arising from the failure of the Cauchy relation C_{14} =C_{44}.It has been suggested for Zinc-blend type crystals, the non-central forces as done by Keating [32] and Martin [105], one finds

$$\omega^2_o = 16/3\ (\mathrm{Ne}2/\mu)\{B^* + 1/6\beta^*)\} \qquad (2.55)$$

Where β^* is a reduced bond bendingforce constant. By considering that dipole interaction contributions to the C_{ij} are described by e_l^{*2} Lucovsky et al [40] have obtained,

$$\beta^* = (C^*_{11} - C^*_{12} - 0.52\, e_l^{*2}) \qquad (2.56)$$

For Zinc-bend type solids el^{*2} can be calculated with the help of equations (2.47),(2.48),(2.55) and (2.56).

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