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EFFECT OF MANY BODY INTERACTIONS ON INDICES OF REFRACTION OF ALKALI HALIDES

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ABSTRACT

A theoretical model for the indices of refraction of alkali halides, incorporating the effect of many body interactions and van der Waals interactions in the framework of rigid shell model is proposed. It is shown to yield accurate values for the indices of refraction of alkali halides. The computed values of indices of refraction of alkali halides are compared with those in literature and measured by other researchers.

Key words : Alkali halides, Rigid shell model, Indices of refraction

INTRODUCTION

The ionic model for crystal indices of refraction assumes that a crystal is composed of distinct polarizable ions, which may be assigned individual polarizabilities. If such a crystal has cubic symmetry, the high frequency indices of refrection, n is related to the polarizabilities of its constituent ions by the Clausius-Mosotti relation

$$\frac{\in -1}{\in +2} = \frac{4\pi\alpha_m}{3v_m} \qquad \ldots(1)$$

Here $\in = n^2$ is the dielectric constant, v_m is the volume per formula unit and α_m is the sum of the polarizabilities of the ions, which compose a formula unit. A more sophisticated approach, developed by Wilson and Curtis [1] and extended and refined by Coker [2], allows the ionic polarizabilities to vary from crystal to crystal in systematic fashion, although at the expense of introducing additional variable empirical parameters. In view of extent of empirical work. [3-7] In this paper, we present a simple interpretation of the

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effect of many body interactions and van der Waals interactions in the framework of rigid shell model for the alkali halides[8].The indices of refraction of alkali halides have been investigated in terms of additional three body interactions term (Z_m, $r_o f_o'$). Z_m and $r_o f_o'$ are determined by several researchers. [9-13] Since some of the vibration frequencies of zone-boundary points have been used to determine the model parameters, therefore, good agreement achieved for symmetry directions does not essentially guarantee the agreement in the other general directions.

Theory

There has been always a continuing effort to obtain accurate interatomic potential functions. The interaction potential energy function is generally used to study the crystalline properties of diatomic crystal like alkali halides. The first alkali halide potential, which gave a good fit to the lattice energy were obtained by Huggins and Mayer in 1933.The total potential for the alkali halides[8] can be written as

$$\Phi = \Phi^{C} + \Phi^{R} + \Phi^{TBI} + \Phi^{VWI} \qquad \ldots(2)$$

Where first term Φ^{C} is coulomb interaction potential and is long-range in nature, second term is Φ^{R} short –range overlap repulsion potential, third termΦ^{TBI} is three-body interactions potential and the last term is Φ^{VWI} , van der Waals interactions potential and owes its origin to the correlations of the electron motions in different atoms. Thus the cohesive energy per mole is given by-

$$\Phi = N\Phi(r) = N(\Phi^{C} + \Phi^{R} + \Phi^{TBI} + \Phi^{VWI}) \qquad \ldots (3)$$

$$\text{Where, } \Phi^{c}(r_0) = -\left[\sum_{n_1,n_2,n_3}^{+\infty} \frac{(-1)^{n_1+n_2+n_3}}{\sqrt{n_1^2+n_2^2+n_3^2}}\right].\frac{e^2}{r_0}$$

$$\Phi^{R} = M\beta_{-+}b\exp\left[(r_+ + r_- - r)/\rho\right] + 1/2M'b\left[\beta_{++}\exp(2r_+/\rho) + \beta_{--}\exp(2r_-/\rho)\right]\exp(-r'/$$

$$\Phi^{TBI} = e^2\sum_{lk}\sum_{l'k'}\sum_{l''k''} Z_k f\{r(lk,l'k')\frac{Z_k''}{|\vec{r}(lk;l''k'')|}$$

$$\Phi_{dd}^{VWI}(r_{ij}) = -\frac{3}{2}\alpha_i\alpha_j\frac{E_iE_j}{E_i+E_j}.\frac{1}{r_{ij}^{6}}$$

Here N is the Avogadro number.

Using the crystal potential expression (2), the equations of motion of two cores and two shells can be written as

$$\omega^2 \underline{M}\,\underline{U} = (\underline{R} + \underline{Z_m}\,\underline{C'}\,\underline{Z_m})\,\underline{U} + (\underline{T} + \underline{Z_m}\,\underline{C'}\,\underline{Y_m})\,\underline{W} \quad \ldots(4)$$

$$O = (\underline{T}^T + \underline{Y_m}\,\underline{C'}\,\underline{Z_m})\,\underline{U} + (\underline{S} + \underline{K} + \underline{Y_m}\,\underline{C'}\,\underline{Y_m})\,\underline{W} \quad \ldots(5)$$

Here U and W are vectors describing the ionic displacements and deformations, respectively. Z_m and Y_m are diagonal matrices of modified ionic charges and shell charges, respectively. The elements of matrix Z_m consists of the parameter Z_m giving the modified ionic charge.

$$Z_m = \{z(z + 12f_0 + 4r_0 f_0')\}^{1/2} \text{ for NaCl} \quad \ldots(6)$$

$$= \{z(z + 16f_0 + 8r_0 f_0')\}^{1/2} \text{ for CsCl} \quad \ldots(7)$$

However, the core and shell charge parameters (X, Y) of RSM will be modified to (Xξ, Yξ). These modifications lead to the following relation :

$$Z_m = Z\xi = X\xi + Y\xi \quad \ldots(8)$$

Such that X + Y = Z; R, T and S are matrices describing various short-range interactions in the crystal. C' is the modified long-range interaction matrix and is given by

$$C' = C + (Z_m^{-2}\, Zr_0\, f_0')\, V + (Z^2\, Z_m^{-2})\, D \quad \ldots(9)$$

Here D is a matrix contributed by the van der Waals interactions.

The elimination of W from equations (4) and (5) leads to the secular determinant :

$$\left|\underline{D}(\vec{q}) - \omega^2\, \underline{M}\,\underline{I}\right| = 0 \quad \ldots(10)$$

Here D (q) is the (6 × 6) dynamical matrix, which is given by –

$$\underline{D}(\vec{q}) = \left(\underline{R'} + \underline{Z}_m \underline{C'} \underline{Z}_m\right) - \left(\underline{T} + \underline{Z}_m \underline{C'} \underline{Y}_m\right) \times \left(\underline{S} + \underline{K} + \underline{Y}_m \underline{C'} \underline{Y}_m\right)^{-1} \left(\underline{T}^T + \underline{Y}_m \underline{C'} \underline{Z}_m\right) \quad \ldots(11)$$

Optical behaviors of alkali halides

As mentioned earlier, the electron-shell deformation is included in form of charge-

transfer in this model, so all the dielectric relations, except the macroscopic Lyddane-Sachs-Teller (LST)-relation, are completely modified. Many body interactions and van der Waals interactions in the framework of rigid shell model, providing more accurate values of several quantities, involved in these relations.

The LST-relation remains unchanged as

$$\frac{\in_0}{\in_\infty} = \left(\frac{\omega_{LO}}{\omega_{TO}}\right)^2 \qquad \ldots(12)$$

Which in turn requires that the values of static and high frequency dielectric constants ($\in_0, \in_\infty$) are given by-

$$\in_\infty = \left[\left\{1+\frac{\alpha_m}{v}\left(\frac{8\pi}{3}+\lambda\right)\right\}\left\{1-\frac{\alpha_m}{v}\left(\frac{4\pi}{3}-\lambda\right)\right\}^{-1}\right] \qquad \ldots(13)$$

$$\in_0 = \left[\left\{1+\frac{\alpha_0}{v}\left(\frac{8\pi}{3}+\lambda\right)\right\}\left\{1-\frac{\alpha_0}{v}\left(\frac{4\pi}{3}-\lambda\right)\right\}^{-1}\right] \qquad \ldots(14)$$

These values of high frequency dielectric constants ($\in_0, \in_\infty$) leads to the following modified Lorentz-Lorentz and Clausius-Mosotti relations are as follows :

$$(L-L)\frac{\in_\infty -1}{\in_\infty +2} = \frac{4\pi\alpha_m}{3v}\left(1+\frac{\lambda\alpha_m}{v}\right)^{-1} \qquad \ldots (15)$$

$$(C-M)\frac{\in_\infty -1}{\in_\infty +2} = \frac{4\pi(\alpha_m+\alpha_I)}{3v}\left\{1+\frac{\lambda(\alpha_m+\alpha_I)}{v}\right\}^{-1} \qquad \ldots (16)$$

Where

$$\lambda = \frac{8\pi pzr_0 f_0'}{9e_L^2} \quad \text{and} \quad \alpha_0 = \alpha_m + \alpha_I .$$

p = 6 (for NaCl) and 12 (for CsCl)

With Lundqvist's effective charge-parameter

$$e_L = \{z(z+12f_0+4r_0f_0')\}^{1/2} \text{ for NaCl} \quad \ldots(17)$$

$$= \{z(z+16f_0+8r_0f_0')\}^{1/2} \text{ for CsCl} \quad \ldots(18)$$

The total electronic polarizabilities of ions are -

$$\alpha_m = \alpha_{m1} + \alpha_{m2} \quad \ldots(19)$$

While ionic polarizabilities are -

$$\alpha_I = \frac{(Z'e)^2}{R_0'} \quad \ldots(20)$$

High frequency dielectric constant -

$$\in_\infty = \left[\left\{1+\frac{\alpha_m}{v}\left(\frac{8\pi}{3}+\lambda\right)\right\}\left\{1-\frac{\alpha_m}{v}\left(\frac{4\pi}{3}-\lambda\right)\right\}^{-1}\right] \quad \ldots(21)$$

Thus the index of refraction is -

$$\text{n} = \left[\left\{1+\frac{\alpha_m}{v}\left(\frac{8\pi}{3}+\lambda\right)\right\}\left\{1-\frac{\alpha_m}{v}\left(\frac{4\pi}{3}-\lambda\right)\right\}^{-1/2}\right] \quad \ldots(22)$$

Besides this, the relation of Ruffa [4] is also modified due to the presence of three-body forces.

Computation

The results of computation are given in Table 1.

RESULTS AND DISCUSSION

Having taken, the van der Waals interactions and three body interactions in the frame work of rigid shell model, we have computed the indices of refraction for alkali halides crystals. The results are presented with the known literature values [5, 14, 15] of indices of refraction in the Table 1.The present values were found to be in a reasonable agreement

with the experimentally known indices of refraction of alkali halides [16-18].

Table 1. Calculated values of indices of refraction and its comparison with both theoretical and experimental data[5, 14 -18]

Solids	Structure	Indices of refraction (Present study)	Indices of refraction[5]	Indices of refraction[14, 15]	Indices of refraction (measured values)[16-18]
LiF	NaCl	1.3892	1.4428	1.0663	1.3915
LiCl	NaCl	1.6703	1.5100	1.3407	1.6620
LiBr	NaCl	1.7944	1.5727	1.5126	1.7840
LiI	NaCl	1.9723	1.7230	1.7675	1.9520
NaF	NaCl	1.3229	1.4918	1.1941	1.3360
NaCl	NaCl	1.5329	1.5681	1.4402	1.5400
NaBr	NaCl	1.6248	1.6120	1.5508	1.6412
NaI	NaCl	1.7549	1.7304	1.8170	1.7745
KF	NaCl	1.3638	1.4779	1.2125	1.3610
KCl	NaCl	1.4832	1.5727	1.4519	1.4900
KBr	NaCl	1.5459	1.6069	1.5379	1.5590
KI	NaCl	1.6370	1.7087	1.7202	1.6770
RbF	NaCl	1.3928	1.4953	1.2599	1.3980
RbCl	NaCl	1.4832	1.5869	1.4879	1.4930
RbBr	NaCl	1.5362	1.6120	1.5508	1.5530
RbI	NaCl	1.6155	1.7087	1.7202	1.6474
CsF	NaCl	1.4690	1.5100	1.2894	1.4830
CsCl	CsCl	1.6124	1.5967	1.4879	1.6100
CsBr	CsCl	–	1.6509	1.5771	1.6700
CsI	CsCl	1.7320	1.6950	1.7357	1.7876

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