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Quantum computation of photoelastic properties of ionic crystals

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Abstract A general scheme for computation of photoelastic properties has been proposed using the well-established quantum ion dependent theory. The families under consideration are I–VII type ionic crystals and AB_2 type cross compounds. The calculated values of strain polarisability constant (λ) for the crystals in these families are compared with the predicted values by some other workers as well as with the available experimental ones. The results of the present work are in much better agreement with the available experimental data than the earlier estimated ones. This formulation is proposed to extend for other families of similar nature and theoretical analysis of the properties of nano materials. The industrial applications are also suggested.

Introduction

The strain derivatives of optical dielectric constant and average energy gap of solids are directly related to their photoelastic behaviours. Application of hydrostatic pressure on the ionic crystals has been a subject of great interest in the last decade since it gives variations in the dielectric constant and refractive index of the materials. The theory is extremely useful in the field of photoconducting properties of crystals, solar cell technology [1], high power laser beams [2, 3], etc. From the knowledge of pressure and volume derivatives of dielectric constants, the volume dependence of energy gap and electro negativity parameters can be satisfactorily analysed [4, 5]. Many theories have come up for presenting dielectric behaviour of strained crystals in order to explain experimental behaviour properly. Out none of the theories has so far given very satisfactory agreement with the experimental results.

Among different efforts, Coker [6] developed Wilson–Curtis function [7] for variation of electronic polarisabilities. This function has been used for evaluation of strain dependence of polarisabilities and refractive indices of alkali halide crystals by Dutta et al. [8] who developed formulation for explaining the electronic polarisabi1ity constant for alkali halides. However, this theory is not capable to explain photoelastic behaviour of strained crystals very properly, since the calculated values do not agree well with the corresponding experimental ones. Also Dutta et al. [8] state that formulation given by Pantelides [9] was not capable of explaining the photoelastic behaviour of alkali halide crystals. However, the present work disagrees greatly with this statement. In fact Pantelides [9] proposed a cation dependent formulation for alkali halide ionic crystals which was extended by Sarkar and Goyal [10] for all ionic and covalent binary crystals in the form of a detailed generalized ion dependent quantum formulation This ion dependent dielectric theory was proved to be of great importance as it gave many satisfactory explanation for the behaviour of strained crystal [11, 12], their heats of formation [13], temperature dependences [14], etc.

Thus, in the present communication we wish to extend the general quantum ion dependent model [10, 13] for the effect of hydrostatic pressure on the dielectric properties of ionic crystals. This analysis produces much better agreement with observed values than obtained in other theories.

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Theory

In simple binary solids as we move from rocksalt to wurtzite, and zinc blend and finally to diamond structures a gradual transition from high ionicity to high covalency takes place [4]. Ion dependent model [10] shows that the dielectric behaviour has gradual change from high cation dependence to high anion dependence for crystals with high ionicity to high covalency.

In order to predict the volume derivatives of simple binary crystals we have used this well-established ion dependent electronic dielectric theory. The relation between high frequency dielectric constant (ε_∞) and inter ionic separation (R) [10] is:

$$\varepsilon_\infty = 1 + BR^S \tag{1}$$

where B is ionic characteristic and S is family characteristic.

The binary crystals under consideration are of the type $A^N B^{8-N}$. This whole group has four distinct families. For $N = 1$–4 we have I–VII, II–VI, III–V and IV–IV families. The I–VII family is purely ionic (alkali halides), II–VI ones have mixed ionic covalent character, III–V ones are mostly covalent while IV–IV ones are purely covalent. In accordance I–VII family shows purely cation dependence with the family characteristic $S = 3$ and cation characteristic B having different constant values for Li, Na, K and Rb compounds.

The volume of unit cell under consideration is given by

$$V = \frac{1}{2} kR^3 \tag{2}$$

where (k) is a constant. Then volume derivative of electronic dielectric constant (ε_∞) is obtained from Eqs. 1 and 2 as:

$$V\frac{\mathrm{d}\varepsilon_\infty}{\mathrm{d}V} = (\varepsilon_\infty - 1)\left[\frac{S}{3} + \frac{V}{B}\left(\frac{\mathrm{d}B}{\mathrm{d}V}\right)\right] \tag{3}$$

The relation between optical refractive index (n) and electronic polarisabi1ity (α) of solid is obtained from well known Lorentz–Lorenz expression [4] as

$$\frac{n^2 - 1}{n^2 + 1} = \frac{4\pi}{3}\sum_i N_i \alpha_i \tag{4}$$

here $N \propto 1/V$ where V is volume per ion pair. Using this Eq. 4, volume derivative of refractive index (n) is obtained [15] as

$$V\frac{\mathrm{d}n}{\mathrm{d}V} = -\frac{(n^2 - 1)(n^2 + 2)}{6n}(1 - \lambda) \tag{5}$$

here the characteristic parameter (λ) is termed as strain polarisability constant.

The optical refractive index (n) is directly related to the electronic dielectric constant (ε_∞) as

$$n^2 = \varepsilon_\infty \tag{6}$$

The two relations 5 and 6 directly leads to

$$\lambda = 1 + \frac{3V(\mathrm{d}\varepsilon_\infty/\mathrm{d}V)}{(n^2 - 1)(n^2 + 1)} \tag{7}$$

From the ion dependent dielectric theory we find the values of dimensionless volume derivative of the ion characteristic B (viz. $(V/B)(\mathrm{d}B/\mathrm{d}V)$) and putting that in

Table 1 Input data and calculated value of λ for solids in the ionic I–VII family along with available experimental values

Name of solids	n (Exp.) [19]	$V(\mathrm{d}\varepsilon_\infty/\mathrm{d}V)$ (Cal.) [16, 17]	λ (Cal. from present model)	λ (Exp.) [6]	λ (from other theories)	
					[7]	[8]
LiF	1.378	−0.366	0.787	0.715	1.021	0.838
LiCl	1.643	−0.690	0.741	–	0.799	0.668
LiBr	1.788	−0.893	0.766	–	0.682	0.576
LiI	1.949	−1.137	0.799	0.768	0.696	0.574
NaF	1.303	−0.448	0.581	0.599	0.893	0.949
NaCl	1.516	−0.897	0.519	0.590	0.746	0.782
NaBr	1.612	−1.104	0.549	0.529	0.688	0.623
NaI	1.760	−1.449	0.594	–	0.703	0.633
KF	1.341	−0.509	0.798	–	0.566	1.049
KCl	1.483	−0.768	0.443	0.490	0.613	0.740
KBr	1.549	−0.896	0.460	0.495	0.560	0.636
KI	1.643	−1.088	0.590	0.504	0.593	0.624
RbF	1.378	−0.565	0.508	–	0.511	1.219
RbCl	1.483	−0.744	0.558	0.396	0.525	0.721
RbBr	1.549	−0.868	0.562	0.381	0.463	0.586
RbI	1.643	−1.054	0.605	0.457	0.531	0.605

Table 2 Input data and calculated value of λ for AB_2 solids

Name of solids	n (Exp.) [11, 19]	$V(\mathrm{d}\varepsilon_\infty/\mathrm{d}V)$ (Cal.) [17, 20]	λ (Cal. from present model)
CaF_2	1.435	−0.57	0.602
$CaCl_2$	1.627	−0.83	0.675
$CaBr_2$	1.811	−1.13	0.718
SrF_2	1.428	−0.88	0.371
$SrCl_2$	1.679	−1.45	0.504
$SrBr_2$	1.835	−1.90	0.552

Eq. 2 the dimensionless volume derivative of electronic dielectric constant ε_∞ (viz. $V(\mathrm{d}\varepsilon_\infty/\mathrm{d}V)$) can be found [16, 17]. Thus, the values of strain polarisability constant λ for different solids in the ionic I–VII family can be calculated from Eq. 7 and are reported in Table 1. Similarly, λ can be calculated for AB_2 solids and are reported in Table 2. This generalised formulation may be applied for estimation of λ for other families.

Results and conclusion

The calculated values of strain polarisability constant (λ) for different solids in the ionic I–VII family and for AB_2 solids calculated from present ion dependent quantum model are reported in Tables 1 and 2, respectively with the necessary input data. View of Table 1 revels that in most of the cases, agreement of the present values is much more satisfactory than those of the others. Only in the case of rubidium compound the values are comparable up to some extent. Similar calculations is made for AB_2 family and reported in Table 2, although experimental values for the compounds in this family are not available.

Dutta et al. [8] started with the equation same as Eq. 5 in the present work but they used other classical considerations. They got the values of λ using Coker [6], Wilson–Curtis [7] and Yamashita–Kurosawa [18] model, and reported that the experimental values of λ in most of the cases are in between the two sets of values calculated from Paulings and Coker's free state polarisabilities. It is interesting to note that none of their calculated values are close to the experimental ones. In Table 1 we include some of their calculated values for comparison.

It is therefore concluded that the present quantum cation dependent approach to the photoelastic behaviour of ionic solids is much more satisfying than any other classical approach [6–8, 18]. The same method may be applied to the covalent III–V solid families with respect to their anion dependent formulation.

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