Effect of Charge Transfer on Phonon Dynamics of Polarizable Materials

RATHORE V.

Department of Engineering Physics, School of Engineering, Chameli Devi Group of Institutions, Indore,
Gram Umrikheda Khandwa Road Near Toll Booth Indore- 452020 M.P. India
Email:dr.vikramrathore36@yahoo.co.in

Abstract

This Paper gives the connection between the polarization of ions and the repulsive force between them. We have investigated the phonon dynamics of Polarizable Materials in NaCl phase using Rigid Shell Model with pair wise interionic interaction potential. The potential consist of the long -range Coulomb and three-body interactions and the short -range van der Waals interaction and the Hafemeister and Flygare type overlap repulsion extended up to the second neighbor ions. The present model basically includes the effect of charge transfer caused by the electron-shell deformation of the overlapping ions in the frame work of both ions polarizable. this takes account of the polarizability of ions for vibrations of all wavelengths. There is generally good agreement between the measured dispersion relations and the dispersion relations calculated on the simple version of the shell model-Coulomb forces between ions of unit charge with the iodine atoms polarizable and central repulsive forces between first neighbors only, acting through the iodine shell. The elastic constants obtained from the model have been used to calculate the phonon dispersion relation in the symmetry direction .

Key Words: lattice dynamics, polarizability, elastic constants, Phonons, Charge Transfer.

Introduction

The lattice dynamics of a crystal is described by a frequency, wave vector dispersion relation, inso-far as it is harmonic. In the last few years it has become possible to determine experimentally this dispersion relation using X-ray diffraction and neutron spectrometry. This dispersion relation has been measured fairly accurately for several metallic and semi conducting crystal consisting of one kind of atom. The only determinations for crystals having more than one kind of atom have been by x-ray diffraction methods. However, there is good reason to believe that neutron measurements are much more accurate than are x-ray measurements for crystals with more than one atom per unit cell. Thus it seems desirable to study such crystals by neutron spectrometry.

In the determination of the dispersion relation by neutron spectrometry energy distributions of initially monoenergetic neutrons are measured after scattering by a single crystal in known orientation. The frequencies ν and wave vector q of the vibrations are inferred from conservation of energy and momentum between the neutrons and single phonons. If the frequencies and wave vectors of the phonons are well defined, then   sharp groups (broadened of course by imperfect resolution) are observed in the neutron energy distributions. The center of a neutron group is taken to define the energy (E') and wave vector (K') of those neutrons, which had interacted with a particular vibration. The frequency and wave vector of the vibration are given by the conservation equations

$$Eo- E'=\pm\ h\nu=\pm\ h\omega,$$
$$Q=Ko- K'=2\pi\tau- q,$$

(1.1.1)

Where Eo and Ko are the energy and momentum of the incident neutrons, and   is any vector of the reciprocal lattice.(for the cubic crystals we shall consider ,)   =(1/a)(h,k,l) where h,k,l are a set of Miller indices and a is the cubic lattice constant)

The Model

The present model basically includes the effect of charge transfer caused by the electron-shell deformation of the overlapping ions in the frame work of both ions polarizable which takes account of the polarizability of ions for vibrations of all wavelengths. The theory is based on a model of an ionic crystal already used by Dick and Over Hauser and by Hanlon and Lawson in studies of the dielectric properties of the lattice vibrations of germanium. Calculations from the model in its simplest form-Coulomb forces between all ions, each having unit (positive or negative) charge, and a short-range central repulsive force between nearest neighbors only-give dispersion curves in good but not complete agreement with the experimental results .

We have determine the dispersion ν (q) relation of the lattice vibrations in the symmetric [001],[110],and [111] directions of sodium iodide at 110 K by the method of neutron spectrometry .The transverse acoustic ,longitudinal acoustic and transverse optic branches were determined completely with a probable error of about 3%.The dispersion relation for the longitudinal optic (LO) branch was determined for the [001] directions with less accuracy. Frequencies of some important phonons with their errors   (units 10^{12} cps) are: TA [0,0,1] 1.22 $\pm$ 0.04, LA [0,0,1] 1.82 $\pm$ 0.06, TA [$\frac{1}{2},\frac{1}{2},\frac{1}{2}$] 1.52 $\pm$ 0.05, LA [$\frac{1}{2},\frac{1}{2},\frac{1}{2}$] 2.32 $\pm$ 0.06:   TO [0,0,0] 3.6 $\pm$ 0.1,:   TO [0,0,1] 3.8 $\pm$ 0.1, TO[$\frac{1}{2},\frac{1}{2},\frac{1}{2}$]3.5 $\pm$ 0.1.These topics

include a discussion of the effects of ionic polarizability on elastic constants, the effect of introducing noncentral interactions and interactions between second neighbors, and a discussion of the properties of crystals in which both ions are polarizable.

Theory of Vibrations of a Lattice of Point Ions

Since the present work is an extension of Kellermann's we begin with a brief summary of his treatment of the problem, at the same time explaining our own notation. We shall find figs.1 (a) and 1(b) useful in defining certain terms. In Kellermann's approximation the atoms are regarded as exerting short – rang "overlap" forces between nearest neighbors only, with Coulomb interactions between ions throughout the crystal. The polarizability of the ion is neglected.

The force between nearest neighbors is taken to be a central force, so that the energy per unit cell is given by

$$Uo = - \alpha_M \frac{Z^2 e^2}{r_0} \quad 6\varphi^R \quad r_0$$

Where α_M is the Made lung constant, $2r_0$ the side of the (cubic) unit cell and Ze the charge on the positive ion (e=+4.803X10^{-10} esu). Two parameters A and B are defined in terms of the derivatives of the overlap potential φ^R by

$$\frac{1}{r_0}\left[\frac{d}{dr}\varphi^R\right]_{=r_0} = \frac{e^2 B}{2v}$$

$$\text{and} \quad \left[\frac{d^2}{dr^2}\varphi^R\right]_{=r_0} = \frac{e^2 A}{2v} \tag{2.1.2}$$

Where $v = 2r_0^3$ is the volume of the (trigonal) unit cell. The appearance of $e^2 2v$ in these definitions is merely a convention which makes A and B of a convenient order of magnitude . Kellermann takes Z=1 throughout his work. We use the superscript (R) to distinguish quantities associated with the repulsive interaction between ions from those associated with Coulomb interaction, for which we use the superscript (C). Kellermann shows that for the static lattice to be in equilibrium,

$$B = \frac{2}{3}\alpha_M Z^2 = -1.165 Z^2$$

and that the elastic constants are given by the expressions

$$c_{11} = \frac{e^2}{4r^{4_0}} A - 2.56 \frac{Ze^2}{2r^{4_0}}$$

$$c_{12} = \frac{e^2}{4r^{4_0}} B + 1.28 \frac{Ze^2}{2r^{4_0}} \qquad (2.1.3)$$

$$c_{44} = 0.696 \frac{Ze^2}{2r^{4_0}}$$

and the compressibility β by

$$\frac{1}{\beta} = \frac{c_{11} + c_{12}}{3} = \frac{e^2}{12r^4} \; A + 2B$$

in general a force constant between atoms of type κ and κ' in unit cells l

and l' will be written as

$$\frac{\partial^2}{\partial x \partial y} \varphi \; {l_k, l_{k'}} = \varphi_{xy^R} \; {l_k, l_{k'}} + z^2 \varphi_{xy^C} \; {l_k, l_{k'}}$$

$\varphi_{xy^R} \; {l_k, l_{k'}}$ Will usually be zero unless the atoms are nearest neighbors. If we take $\kappa = 1$ to denote the positive ions and label the unit cells as shown in fig. 1(a) it follows from these definitions that

$$\varphi_{xx^R} \; 01,02 = \varphi_{yy^R} \; 01,02 = etc = \frac{e^2 B}{2v}$$

And $\quad \varphi_{xx^R} \; 01,02 = \varphi_{xx^R} \; 01,02 = etc = \frac{e^2 B}{2v}$ $\qquad\qquad$ (2.1.4)

Other force constant s such as $\varphi_{xy^R} \; 01,02$ are identically zero.

In a lattice vibration, the displacement $u \; lk$ of an atom from its equilibrium position $r \; lk$, due to a

normal mode of wave vector q $q = \frac{2\pi}{\lambda}$ and circular frequency ω is given by

$$u\ l,\kappa = U\ \kappa\ \exp i\ q\ .\ r\ lk - \omega t$$

(2.1.5)

The direction of U specifies the polarization of the mode (note that polarization frequently occurs with another meaning). We now define quantities, to which we shall refer as coefficients,

$$R_{xy}\ \kappa\kappa = -\sum \varphi_{xy^R}\ l_\kappa, l_{\kappa'} \times \exp\left\{ iq\ .\ \left[r\ l',k' - r\ lk \right] \right\}$$

$$C_{xy}\ \kappa\kappa = -\sum \varphi_{xy^R}\ l_\kappa, l_{\kappa'} \times \exp\left\{ iq\ .\ \left[r\ l',k' - r\ lk \right] \right\}$$

General Theory with Polarizable Ions

The connection between the polarization of ions and the repulsive force between them has recently been considered by Yamashita and Kurosawa by Dick and Overhauser, and by Hanlon and Lawson. These latter authors have independently suggested a shell model for an ion having a closed electron configuration. Their models are somewhat different, particularly as to the charge in the shell, which represents the outer electrons We have used this model with certain extensions in an attempt to give an improved theory of the lattice dynamics of ionic crystals. A simple version of the theory which applies when only the negative ion is polarizable is found to be in fairly good agreement with our experimental results for sodium iodide .The general treatment Is applicable to any diatomic cubic crystal in which the surroundings of each ion have tetrahedral symmetry, and therefore includes NaCl, CsCl. ZnS and isomorphous structures. The theory remains within the framework of the Born-von Karman theory; in particular both the harmonic and the adiabatic approximations are utilized. In the Born-von Karman theory the energy perturbation in the lattice is written

$$\varphi_2 = -\frac{1}{2}\sum\sum\sum \varphi_{xy}\ lk,l'k'\ u_x\ lk\ u_y\ l'k'\ ,$$

(2.2.1)

where for an alkali halide k assumes the values 1 and 2 The equations of motion

$$m_k u_x\ lk = -\partial\varphi_2\partial u_x\ lk\ ,$$

then lead to Esq.(2.1.9).The summation .(2.2.1).is now extended over four values of k,k=3 denoting the shell of the positive ion ,k=4 that of the negative ion while indices 1 and 2 refer to the corresponding cores .The charge in a particular unit k (core or shell) is taken as $X_1 e, \ X_2 e \ , Y_1 e \ , Y_2 e$,for k=1,2,3

and 4 respectively. The charge on the positive ion is then $Z_1 e = X_1 + Y_1 e,$ and on the negative ion , $Z_2 e = X_2 + Y_2 e,$ while $Z_1 + Z_2 = 0$

The force constants coupling a shell isotropically to the core of the same atom are denoted by k_1 and k_2 for the positive and negative ions respectively. The polarizability of a free negative ion is then $\dfrac{Y_{2^2} e^2}{k_2}$ we shall find, however, that its value is reduced in the crystal. Separate symbols for the short-range force constants are introduced as follows:

$\varphi_{xy^s} \; l3,l' \, 4$ between the shells

$\varphi_{xy^D} \; l1,l' \, 2$ between the cores

$\varphi_{xy^F} \; l1,l' \, 4$ core of positive to shell of negative ion,

$\varphi_{xy^F} \; l3,l' \, 2$ shell of positive to core of negative ion

Although it is not dictated by the physics of the problem, we propose to assume that the two latter force constants are equal. This makes the interaction between two ions completely symmetrical and simplifies the analysis besides being physically not unreasonable.

It will be noticed that these Esq. are somewhat more symmetrical from which they were derived. Equations(2.2.1) could, in fact have been derived in another way which consists in expressing the energy perturbation [φ_2 of Eq.(2.2.1)]as a quadratic function of the nuclear displacements $u \, lk$ and the atomic dipole moments $p \, lk$ .Topoygo and Mashkevich and Tolpygo have given a wave-mechanical justification for this procedure, using the tight-binding approximation. Their analysis was not taken in a direction that would lead to Eqs.(2.2.1) however ,and their expression for the energy perturbation does not include terms which correspond to the coefficient S in Eqs.(2.2.1).A theory resembling that of Mashkevichn and Tolpygo in some respect has also been proposed by Yamashita and Kurosawa. Equations may be derived in a purely phenomenological way by postulating an expression for the energy perturbation φ_2 of the form

$$\varphi_{xy^R}\ lk,l'k'\ u_x\ lk\ u_y\ l'k'\ +\varphi_{xy^T}\ lk,l'k'\left[\frac{u_x\ lk\ p_y\ l'k'}{Y_{k'}e}\quad\frac{p_x\ lk\ u_y\ l'k'}{Y_k e}\right]$$

$$\frac{1}{Y_k Y_{k'} e^2}\varphi_{xy^S}\ lk,l'k'\ p_x\ lk\ p_y\ l'k'\quad\frac{1}{2}\sum\left\{\frac{1}{\alpha_k}p_{x^2}\ lk-\left[p_x\ lk\ +Z_k eu_x\ lk\ \right]E_x\ lk\right\}. \qquad (2.2.9)$$

$$\varphi_2=-\frac{1}{2}\sum\sum\{\}\{\}$$

Here E(lk) is the effective field at r(lk) and α_k is the polarizability that an atom of k would have in the absence of short-range interaction between the dipoles (that is ,when $\varphi_{xy^S}= 0$).The actual polarizability of the atom in the crystal is not quite the same as α_k .Further discussion of this point will be found in Appendix 3.This constants Y_k are now to be regarded simply as normalizing factors when they are equal they could be incorporated in the "generalized force constants" φ_{xy^T} and φ_{xy^S} to give an expression completely symmetrical in u and in p, the coordinates and dipole moments .Use of the expression(2.2.9) with the equations of motion given by Mashkevich and Tolpygo

$$m_k u_x\ lk\ =-\frac{\partial\varphi_2}{\partial u_x\ lk}\ ,\quad 0=\frac{\partial\varphi_2}{\partial p_x\ lk}\quad\text{leads eventually to Eqs.(2.2.5).}$$

However derived Eqs.(2.2.7) provide in principal a solution of the problem, for on elimination of W(1) and W(2) we obtain two equations which may be written

$$m_1\omega^2 U\ 1\ =A\ 11\ U\ 1\ +A\ 12\ U\ 2\ , \qquad\qquad (2.2.10)$$

$$m_2\omega^2 U\ 2\ =A\ 12\ U\ 1\ +A\ 22\ U\ 2\ ,$$

leading to the characteristic equation

$$\begin{vmatrix} A\ 11-m_1\omega^2 & A\ 12 \\ A\ 12 & A\ 22-m_2\omega^2 \end{vmatrix}=0 \qquad\qquad (2.2.11)$$

If the applied field is of such high frequency that the cores do not move, the term α_I does not appear .This enables us to identify α and α_I ,respectively, as the electronic polarizability of the negative ion ,and the ionic polarizability of the content of one unit cell. The electronic polarizability is related to the high frequency dielectric constant ε by

$$\frac{4\pi\alpha}{3v} = \frac{\varepsilon-1}{\varepsilon+2} \tag{2.3.12}$$

while the static dielectric constant ε_0 is similarly related to the total polarizabilty ,that is

$$\frac{4\pi \; \alpha+\alpha_I}{3v} = \frac{\varepsilon_0-1}{\varepsilon_0 \; 2} \tag{2.3.13}$$

When these results are used to eliminate α and α_I from Eq.(2.3.10),the equation reduces to $\omega_{L^2}/\omega_{T^2} = \varepsilon_0/\varepsilon$.

When both ions are polarizable the derivation is more cumbersome, but the same final result is obtained.

Calculations of Dispersion Curves

We have computed dispersion curves in the three symmetric directions [100],[111],and [110],on the basis of the two models previously discussed-the point ion model ,and the shell model with one ion only polarizable,and forces acting through the shell. The calculated curves are shown in fig2 together with experimental points to be discussed later. In the calculations on the point ion model the single disposable parameter was fixed by means of the elastic constant c_{11} . In the calculations on the shell model the three disposable parameters, selected to be $R_0=S_0$,d and αv ,were fixed by means of c_{11} .and the high –and low –frequency dielectric constants , ε and ε_0 ,by using given Equations In addition the experimental value of the lattice constant $2r_0$ was used).The values used are shown in Table II. The value taken for c_{11} when the computations were carried out was slightly smaller than the best value now obtainable, based on the measurements of Dalven and Garland.[25] The dielectric constants were taken from a compilation by Born and Huang.[16] In Table III the elastic constants, dielectric constants, and infrared absorption frequency $\omega_{T \; q=0}$,[16] as measured and as computed on the shell model ,are compared. The

differences in the values of $\omega_{T\,q=0}$ are compatible with the changes with temperature found experimentally for other materials like NaCl and KCl .[26]

Discussion

There is generally good agreement between the measured dispersion relations and the dispersion relations calculated on the simple version of the shell model-Coulomb forces between ions of unit charge with the iodine atoms polarizable and central repulsive forces between first neighbors only, acting through the iodine shell. The root-mean-square deviation between theory and experiment is about 7%. In assessing this agreement it should be recalled that no free parameters were used to fit the neutron data, the parameters of the model being fixed by the elastic constant c_{11} and by the high and low frequency dielectric constants. We consider that the agreement verifies that the general picture is correct

There are, however, real discrepancies existing between theory and experiment, especially in the LA mode near the zone boundary in the [111] direction (the point $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).It would be of interest to try to assign physical origins to these discrepancies and thus to see in what ways the simple model could be improved

One significant fact is that on the acoustic branches the experimental points in every case lies between the curves for the point ion model and the shell model, although they are closer to the latter. Thus these branches seem to be overcorrected for the effects of polarizability. On the simple model this could only be improved at the price of no longer fitting the dielectric constants and violating the theorem (strongly based on macroscopic theory) that the ratio of the longitudinal and transverse optic frequencies at $q=0$ is equal to ($\varepsilon_0\varepsilon^{\frac{1}{2}}$) Some modifications to the model itself are there fore indicated.

A possible modification is suggested by the discrepancy in the mode LA $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The iodine ions in Polarizable Material like NaI are much larger (ionic radius 2.20A) than the sodium ions (1.00A) [32] and it is quite likely that there is a small direct interaction between nearest neighbor iodine ions .In the mode LA $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ only the iodine ions move, near (like) neighbors against each other. The sodium ions remain fixed as a consequence of symmetry. It is there fore reasonable that this frequency should be raised by a small iodine-iodine interaction.

If, however, we simply introduce second neighbor force constants between iodine ions (Appendix A2) to reconcile theory and experiment for LA $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ then the agreement is made worse at other points and other small changes are necessary. One such change is the introduction of non-central forces between first neighbors such non-central forces are thought to be small.

References

[1]   R.K.Singh, Phys.Rep.85 259 (1982).

[2]   J.M.Leger et al.,Phy.Lett.A80 325 (1980).

[3] J.A. Jackman,T.M.Holden.W.J.L.Buyers,P.de V Duplessis,O.Vogt and J.Genossar,Phys . . . Rev.B33 7144 (1986).

[4] Dinesh Varshney,N,Kaurav,R.Kinge and R.K.Singh, J.Phy:Condens.Matter s.19 23624 (2007).

[5] Dinesh Varshney,R.Kinge, N,Kaurav,S Shah and R.K.Singh, High Pres. R