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Dielectric Properties and Different Models of Ionic Crystals

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The dielectric properties of ionic crystals are discussed according to the various models so far proposed. To test Szigeti's relation on compressibility, the problem of the most suitable formula to account for the second-neighbor and many-body interactions is carefully discussed. Two different models for many-body interactions are considered. It is found that results are quite sensitive to the models of many-body interactions. From the corrected values of the Szigeti constant it is concluded that the shell model is good for some ionic crystals, while for others the deformation-dipole model may be better.

I. INTRODUCTION

Recently, Lowndes and Martin[1] have made careful measurement of the dielectric constants of a large number of alkali halide crystals at low temperature. They have compared the results of their measurement with some of the existing models of ionic crystals and have noted some discrepancies. For the purpose of comparison they used the two well-known Szigeti relations. The first of these relations correlates the two dielectric constants ϵ_0 and ϵ_∞ with the long-wavelength transverse optical frequency ω_0. The second relation correlates ϵ_0, ϵ_∞, and ω_0 with $\bar{\beta}$, the harmonic compressibility of the crystal. The two relations may be written in the form

$$S_1 = \frac{(\mu \mathfrak{v}_0)^{1/2}}{Ze} \; \frac{3\omega_0}{\epsilon_\infty + 2} \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi}\right)^{1/2} , \tag{1}$$

$$S_2 = A \; \frac{\beta^*}{\bar{\beta}} \; , \quad \beta^* = \frac{3\mathfrak{v}_0}{\mu r_0^2} \left(\frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\right) \frac{1}{\omega_0^2} \; , \tag{2}$$

where Ze is the ionic charge, μ is the reduced mass, $\mathfrak{v}_0$ is the volume of the unit cell, and r_0 is the harmonic value of the nearest-neighbor separation. A is a correction factor for many-body and second-neighbor non-Coulomb interactions. If non-Coulomb interactions are central and confined to nearest neighbors only, then $A = 1$. The right-hand expressions in both the equations are dimensionless quantities and can be calculated from the experimental values of ϵ_0, etc., provided that the correction factor A is known.

The predicted values of S_1 and S_2 are strongly model dependent. It is for this reason that relations (1) and (2) may be used for critically testing the validity of a particular model. If ions are assumed to be polarizable by an electric field only and interactions are confined to the second nearest neighbors, then both S_1 and S_2 are equal to unity. The experimental values of S_1 are, however, less than 1. The deviation can be explained either by introducing an additional dipole moment for each ion pair because of a redistribution of the charge cloud due to overlap and due to the nonuniformity of the Coulomb field of the nearest neighbors (deformation-dipole model[2]) or by a shell model.[3]

The constant S_2 is predicted to have a value equal to unity in the deformation-dipole model. But the shell model predicts $S_2 > 1$. Lowndes and Martin,[1] using a suitable estimate of the correction factor A, found that the experimental values of S_2 are less than 1 in all cases. This contradicts the prediction of both the shell model and the deformation-dipole model. Recently Roy, Basu, and Sengupta[4] have shown that the deformable-shell-model[5] calculations give fairly good values of ω_0 with interaction parameters which are consistent with the dielectric and elastic data. This means that both the relations (1) and (2) can be consistently explained on the basis of the deformable-shell model.

On a critical examination of the correction factor A used by Lowndes and Martin,[1] we find that there is an error in the formula in which the second-neighbor interaction is accounted for. Moreover, the many-body correction in A comes out with opposite sign if instead of the angle-dependent many-body interaction one uses other forms, such as is implied in the deformable-shell model[5] or the breathing-shell model.[6,7] Again Lowndes and Martin[1] use, instead of the harmonic values, the zero-degree values of both the dielectric and elastic data. For ϵ_0, ϵ_∞, and ω_0 this will not introduce any serious error. But for the elastic data the difference is considerable both in $\tilde{C}_{12}-\tilde{C}_{44}$ and in $\tilde{\beta}$.

In view of the above anomalies we propose to examine Szigeti's relation on compressibility more carefully. In Sec. II we discuss the theory of long-wavelength optical vibrations according to the several models that have been suggested for the ionic crystals, and calculate the predicted values of the constant S_2. It is found that the (both-ions-polarizable-shell) model, deformable-shell model, and breathing-shell model all predict S_2 to be greater than unity.

The question of finding the most suitable formula for the correction factor A is discussed in Sec. III. It is found that the correction due to many-body interaction can be carried out using experimental values of $\tilde{C}_{12}-\tilde{C}_{44}$ and $\tilde{\beta}$, so that uncertainties due to the differences in the estimates of overlap-potential parameters can be eliminated. The sign of the correction term, however, depends on whether we are using effectively angle-dependent many-body interactions or not. The correction due to the second-neighbor van der Waals and overlap interaction is carried out by a formula which is insensitive to small variations in the parameters of the overlap potential. Calculated values of S_2 are given in Sec. IV and the results are compared with the predictions of the different models.

II. LONG-WAVELENGTH OPTICAL VIBRATIONS IN VARIOUS MODELS

The macroscopic theory of long-wavelength optical vibrations of ionic crystals has been discussed by Huang (see Born and Huang[8]) in terms of the three macroscopic quantities $\vec{E}$, the electric field, $\vec{P}$, the polarization, and $\vec{W}=(\mu/\upsilon_0)^{1/2}(\vec{x}_+-\vec{x}_-)$, where $\vec{x}_+-\vec{x}_-$ is the change in the equilibrium separation between the positive and the negative ions. The basic equations are written in the form

$$\ddot{\vec{W}}=b_{11}\vec{W}+b_{12}\vec{E}\ ,$$
$$\vec{P}=b_{12}\vec{W}+b_{22}\vec{E}\ . \tag{3}$$

The three constants b_{11}, b_{12}, and b_{22} can be expressed in terms of ϵ_0, ϵ_∞, and ω_0. Using these relations, we can write

$$S_1=\frac{b_{12}}{1+\frac{4}{3}\pi b_{22}}\ \frac{(\mu\upsilon_0)^{1/2}}{Ze}\ ,$$
$$S_2=\frac{3\upsilon_0}{\mu r_0^2}\left(\frac{4\pi b_{22}+3}{\omega_0^2(4\pi b_{22}+3)+4\pi b_{12}^2}\right)\frac{A}{\tilde{\beta}}\ . \tag{4}$$

For any microscopic model, b_{12}, b_{22}, and $\tilde{\beta}$ can be expressed in terms of the parameters of the model, and substituting these in the above equations, we get the values of S_1 and S_2 predicted by the model.

A. Deformation-Dipole Model

This model was proposed by Szigeti[2] in connection with the dielectric properties of ionic crystals. Later it was extended by Hardy[9] and Karo and Hardy[10] to the study of lattice dynamics. The model assumes a distortion dipole moment $m_d(r)$ between a pair of nearest neighbors separated by a distance r. The dipole is measured positive from negative to the positive ion. Without making any further assumption about the nature of the interaction between the ions, one gets (see Born and Huang[8])

$$S_1=1+\frac{n}{3Ze}\left(m_d'(r_0)+\frac{2}{r_0}\ m_d(r_0)\right)\ ,$$
$$\beta^*=3\upsilon_0/Kr_0^2\ , \tag{5}$$

where n is the number of nearest neighbors and K is the isotropic spring constant per unit displacement of an ion due to an interaction other than the Coulomb interaction. For long-wavelength optical vibrations, second neighbors do not contribute to K. Neglecting the third and higher neighbors and assuming only a central interaction $\phi(r)$, we get

$$K=\tfrac{1}{3}n[\phi''(r_0)+(2/r_0)\,\phi''(r_0)]\ . \tag{6}$$

To get an expression for S_2 we write the cohesive energy per unit cell

$$U=n\,\phi(r_0)-\alpha(Ze)^2/r_0\ , \tag{7}$$

where α is the Madelung constant. Using Eq. (7), we get

$$\frac{1}{\tilde{\beta}}=\frac{r_0^2}{9\upsilon_0}\ \frac{d^2U}{dr_0^2}=\frac{nr_0^2}{9\upsilon_0}\left(\phi''(r_0)+\frac{2}{r_0}\ \phi'(r_0)\right)\ . \tag{8}$$

In the above we have used the equilibrium condition $\partial U/\partial r_0=0$. Since we have neglected both the many-body and second-neighbor interaction, we have $A=1$ and

$$S_2=A\,\beta^*/\tilde{\beta}=1\ . \tag{9}$$

B. Both-Ions-Polarizable-Shell Model

This model was first discussed by Dick and Overhauser,[11] who also included an exchange polarization of the charge cloud. We shall neglect the second effect, which in essence is identical to a deformation-dipole model discussed above. Let M_1, $\vec{u}_1^c$, $\vec{u}_1^s$, $-Y_1e$, and K_1 be the mass, the displacement of the core from the equilibrium position, the corresponding quantity for the shell, the shell charge, and the core-shell spring constant of the positive ion of charge $Z_1e=+Ze$, and let the corresponding quantities for the negative ion of charge $Z_2e=-Ze$ be denoted by M_2, etc.; then using the adiabatic condition, the basic equations of the system may be written

$$M_i \ddot{\vec{u}}_i^c = -K_i(\vec{u}_i^c - \vec{u}_i^s) + (Z_i + Y_i)\, e\, \vec{E}_{eff} ,$$

$$0 = K_i(\vec{u}_i^c - \vec{u}_i^s) - K(\vec{u}_i^s - \vec{u}_j^s) - Y_i\, e\, \vec{E}_{eff} ,$$

$$P = \frac{1}{v_0} \sum_{i=1,2} [(Z_i + Y_i)\, e\, \vec{u}_i^c - Y_i\, e\, \vec{u}_i^s] , \tag{10}$$

$$\vec{E}_{eff} = \vec{E} + \tfrac{4}{3}\pi \vec{P} ,$$

$$i = 1, 2, \qquad i \neq j .$$

In the above K has the same meaning as in Eq. (5). Eliminating the shell variables and writing $\vec{W} = (\mu/v_0)^{1/2}(\vec{u}_1^c - \vec{u}_2^c)$, we can transform Eq. (10) to the form of Eq. (3) and thus obtain the values of b_{11}, etc. Using the expression for $\tilde{\beta}$ given by Eq. (8), we get (taking $A = 1$)

$$S_1 = 1 - \frac{K K_1 K_2}{b}\left(\frac{Y_2}{K_2} - \frac{Y_1}{K_1}\right) ,$$

$$S_2 = \left(1 + \frac{K}{K_1} + \frac{K}{K_2}\right) , \tag{11}$$

$$b = K K_1 + K K_2 + K_1 K_2 .$$

Usually $Y_2/K_2 > Y_1/K_1$. Hence $S_1 < 1$ and, since K, K_1, and K_2 are all positive quantities, $S_2 > 1$. Lowndes and Martin[1] have remarked that refinements of the shell model can make S_2 less than unity. Equation (11), however, shows that this is impossible, provided the definition of S_2 is the same as in Eq. (2).

In the Dick-Overhauser model[11] an exchange-polarization effect leads to a deformation dipole between a pair of ions given by[12]

$$m_d(r) = \frac{r_2 - r_1}{r_2 + r_1}\,\frac{1}{2\gamma}\, r^2 \phi(r) , \tag{12}$$

where r_1 and r_2 are the radii of the negative and positive ions, respectively, and γ is an empirical constant whose value was taken to be 1.4 for Na, K, and Rb halides by Dick and Overhauser.[11] Thus in this model we shall have an additional term for S_1 in Eq. (11) similar to that given in Eq. (5), while S_2 is given by the same expression as in Eq. (11).

C. Breathing-Shell Model

In this model Schroder[6] and Nusslein and Schroder[7] introduce effectively many-body interactions[13] by assuming a new degree of freedom, the so-called breathing motion of the shell. The breathing motion is coupled to the shell displacement through the vector D (see Ref. 7). But for long wavelengths, as the wave vector $q \to 0$, $D \to 0$, showing that the breathing motion is decoupled from the shell displacements. In this limit, therefore, the shell displacements are unaffected by breathing and the basic equations for optical vibrations will be the same as in the shell model and Eq. (11) for the Szigeti constants will remain valid.

D. Deformable-Shell Model

In this model proposed by Basu and Sengupta,[5] many-body interactions arising from the deformability of the ion shells are considered. Here many-body force constants are between the second neighbors which become ineffective for long-wavelength optical vibrations. Hence in this model also the shell-model equations for optical vibrations remain valid and Szigeti relations are the same as in Eq. (11).

In the last three models, however, it is well known that many-body interactions are included. Hence in these models, the correction factor A in Eq. (2) will be different from that in shell model where A includes only the second-neighbor interaction. The evaluation of the correction factor for different models is discussed in Sec. III.

III. CORRECTION FACTOR FOR SECOND-NEIGHBOR AND MANY-BODY INTERACTIONS

Let us write the correction factor $A = A_1/A_2$, where A_1 and A_2 are defined by

$$\beta^{*\prime} = A_1 \beta^* , \quad \tilde{\beta}_{nn} = A_2 \tilde{\beta} , \tag{13}$$

where β^* and $\tilde{\beta}$ are the experimental values of the quantities, while $\beta^{*\prime}$ and $\tilde{\beta}_{nn}$ are the values that would result if many-body and second-neighbor interactions are neglected. The correction to β^* is essentially due to the correction in the spring constant [see Eq. (5)]. Since the second-neighbor interaction does not contribute to K, the correction to β^* arises solely from the contribution of many-body interaction to the spring constant. This contribution may be written in the form

$$K_m = -2(\alpha_1 + 2\beta_1) \text{ for NaCl structure ,} \tag{14}$$

where α_1 and β_1 are the axial and radial elements of the nearest-neighbor force constant due to many-body interactions (see Leibfried and Ludwig[14]).

To get the correction factor A_1, we write Eq. (5) in the form

$$\frac{1}{\beta^*} = \frac{1}{\beta^{*\prime}} + \frac{r_0^2}{3v_0} K_m . \tag{15}$$

Multiplying both sides by β^*, we get

$$\frac{1}{A_1} = \frac{\beta^*}{\beta^{*\prime}} = 1 - \frac{r_0^2}{3v_0} K_m \beta^* . \tag{16}$$

The correction factor A_2 will depend on both the second-neighbor and many-body interactions. If the contributions from the overlap and the van der Waals interactions are represented by $U_{nn}(r)$ and $U_{nnn}(r)$ for the nearest and the next nearest neighbors, respectively, the Madelung energy by $U_M(r)$, and the many-body energy by $U_{mb}(r)$ (r is the nearest-neighbor distance), then we write for the cohesive energy per unit cell

$$U(r)=U_{\mathrm{nn}}+U_{\mathrm{nnn}}+U_M+U_{mb}\ . \tag{17}$$

The harmonic compressibility $\tilde{\beta}$ is given by

$$1/\tilde{\beta}=DU(r)=D(U_{\mathrm{nn}}+U_{\mathrm{nnn}})+DU_M+DU_{mb}\ , \tag{18}$$

where

$$D=\frac{r_0^2}{3\mathcal{V}_0}\left(\frac{d^2}{dr^2}-\frac{2}{r_0}\frac{d}{dr}\right)\ . \tag{19}$$

Using the equilibrium condition, we may write

$$DU_M=-\frac{4r_0}{9\mathcal{V}_0}U'_M=\frac{4r_0}{9\mathcal{V}_0}(U'_{\mathrm{nn}}+U'_{\mathrm{nnn}}+U'_{mb})\ . \tag{20}$$

Substituting in Eq. (18), we get

$$\frac{1}{\tilde{\beta}}=\frac{1}{\tilde{\beta}_{\mathrm{nn}}}+\frac{r_0^2}{9\mathcal{V}_0}\left(U''_{mb}+\frac{2}{r_0}U'_{mb}\right)+\frac{r_0^2}{9\mathcal{V}_0}\left(U''_{\mathrm{nnn}}+\frac{2}{r_0}U'_{\mathrm{nnn}}\right) \tag{21}$$

and

$$\frac{1}{A_2}=1-\frac{r_0^2}{9\mathcal{V}_0}\left(U''_{mb}+\frac{2}{r_0}U'_{mb}\right)\tilde{\beta}-\frac{r_0^2}{9\mathcal{V}_0}\left(U''_{\mathrm{nnn}}+\frac{2}{r_0}U'_{\mathrm{nnn}}\right)\tilde{\beta}\ . \tag{22}$$

Even if we neglect the many-body part, Eq. (21) differs from that given by Lowndes and Martin.[1] The reason for the difference is in the definition of $\tilde{\beta}_{\mathrm{nn}}$ which they have used. They define $1/\tilde{\beta}_{\mathrm{nn}}$ by $D(U_{\mathrm{nn}}+U_M)$. But DU_M contains a contribution from the next nearest neighbor [Eq. (20)], and the definition is therefore wrong. In the evaluation of the correction factor by Eq. (22), only the contribution from the next nearest neighbors needs to be estimated. The formula used in Ref. 1 requires, in addition, the estimate of $\tilde{\beta}_{\mathrm{nn}}$ from the short-range-interaction parameters. As the parameters are to some extent uncertain, we have tried to make a minimum use of them. Using Eqs. (16) and (22), we can find the correction factor A for specific models of many-body interaction.

The three-body interaction discussed by Sarkar and Sengupta[16] depends only on the relative separation of the common nearest neighbors. If the overlap interaction is taken in the form $\phi(r)=be^{-r/\rho}$, for NaCl structure the three-body force constants for nearest neighbors are given by

$$\alpha_1=-\frac{4}{\rho^2}A(r_0)\ ,\quad \beta_1=\frac{5}{\rho r_0}A(r_0)\ , \tag{23}$$

where $A(r)=[A(1)+A(2)]e^{-2r/\rho}$, and $A(1)$ and $A(2)$ are the parameters of the three-body interaction. The complete expression for the elastic constants are given by (for NaCl structure)

$$\tilde{C}_{11}=\frac{\phi''}{r_0}-\frac{\phi'}{r_0^2}-1.569\,\frac{e^2}{r_0^4}+\left(\frac{6}{\rho^2 r_0}+\frac{5}{\rho r_0^2}\right)A(r_0)\ ,$$

$$\tilde{C}_{12}=0.348\,\frac{e^2}{r_0^4}+\frac{2}{\rho^2 r_0}A(r_0)\ ,$$

$$\tilde{C}_{44}=0.348\,\frac{e^2}{r_0^4}\ . \tag{24}$$

The cohesive energy per unit cell is given by,[16] neglecting contributions from the second neighbor,

$$U(r)=6\phi(r)-1.748\,e^2/r+15A(r)\ . \tag{25}$$

If we use the equilibrium condition to eliminate ϕ' from the expression for $\tilde{C}_{11}$, we get

$$\tilde{C}_{11}=\frac{\phi''}{r_0}-1.278\,\frac{e^2}{r_0^4}+\frac{6}{\rho^2 r_0}A(r_0)\ . \tag{24'}$$

Using the above results, we get from Eqs. (16) and (22) for NaCl structure

$$\frac{1}{A_1}=1+\frac{2}{3}\left(1-\frac{7}{3}\frac{\rho}{r_0}\right)(\tilde{C}_{44}-\tilde{C}_{12})\beta^*\ ,$$

$$\frac{1}{A_2}=1+\frac{5}{3}\left(1-\frac{\rho}{r_0}\right)(\tilde{C}_{44}-\tilde{C}_{12})\tilde{\beta}-\frac{1}{18r_0}\left(U''_{\mathrm{nnn}}+\frac{2}{r_0}U'_{\mathrm{nnn}}\right)\tilde{\beta}\ . \tag{26}$$

Since $\rho/r_0\ll 1$ and $\tilde{\beta}\simeq\beta^*$, we get for the correction factor

$$A=\frac{A_1}{A_2}\simeq 1+(\tilde{C}_{44}-\tilde{C}_{12})\tilde{\beta}-\frac{1}{18r_0}\left(U''_{\mathrm{nnn}}+\frac{2}{r_0}U'_{\mathrm{nnn}}\right)\tilde{\beta}\ . \tag{26'}$$

The approximate expression (26′) is valid only if the correction terms are small compared to unity. In some cases this condition is not fulfilled and the exact expression for A should be used.

Simplifying Lowdin's expression for the lattice energy, Lundqvist[15] has given an expression for a three-body interaction which is proportional to the square of the overlap integral between the nearest neighbors. The contribution to the lattice energy from this three-body interaction may be written in the form

$$\Phi_{mb}=\sum_{\substack{l'\,l''\\k'\,k''}}{}' \sum_{lk\neq l'k',\,l''k''}\frac{e_k e_{k'}}{r\binom{l\ \ l'}{k\ \ k'}}\,f\left(r\binom{l'\ \ l''}{k'\ \ k''}\right)\ , \tag{27}$$

where e_k is the charge of the k ion, and the function f depends on the overlap integral and vanishes unless $l'\,k'$ and $l''\,k''$ are nearest neighbors. We have neglected a small angle-dependent correction term which was later added by Lundqvist. The nearest-neighbor force constants from the above energy are given by

$$\alpha_1=2e^2\,\frac{\alpha-1}{r_0}f''(r_0)+\frac{3.5\,e^2}{r_0^2}f'(r_0)+\frac{20\,e^2}{r_0^3}f(r_0)\ ,$$

$$\beta_1=2e^2\,\frac{\alpha-1}{r_0^2}f'(r_0)-\frac{1.4\,e^2}{r_0^2}f'(r_0)-\frac{10\,e^2}{r_0^3}f(r_0)\ . \tag{28}$$

The elastic constants are given by

$$\tilde{C}_{11}=\frac{\phi''}{r_0}-1.278\,\frac{e^2}{r_0^4}-1.496\,\frac{e^2}{r_0^2}f''$$

$$-1.67\,\frac{e^2}{r_0^3}f'-11.32\,\frac{e^2}{r_0^4}f\,,$$

$$\tilde{C}_{12}=0.348\,\frac{e^2}{r_0^4}+2.330\,\frac{e^2}{r_0^3}f'+4.173\,\frac{e^2}{r_0^4}f\,,$$

$$\tilde{C}_{44}=0.348\,\frac{e^2}{r_0^4}+4.173\,\frac{e^2}{r_0^4}f\,, \tag{29}$$

and the cohesive energy per unit cell is given by

$$U(r)=6\phi(r)-1.748\,\frac{e^2}{r}-8.976\,\frac{e^2}{r}f(r)\,. \tag{30}$$

Using the above results, we get from Eqs. (16) and (22)

$$\frac{1}{A_1}=1+0.499\,\frac{e^2}{r_0^2}f''\beta^*-0.52\,(\tilde{C}_{44}-\tilde{C}_{12})\,\beta^*\,,$$

$$\frac{1}{A_2}=1+0.499\,\frac{e^2}{r_0^2}f''\tilde{\beta}-\frac{1}{18r_0}\left(U''_{\rm nnn}+\frac{2}{r_0}U'_{\rm nnn}\right)\tilde{\beta}\,, \tag{31}$$

and

$$A=\frac{A_1}{A_2}\simeq 1+0.52\,(\tilde{C}_{44}-\tilde{C}_{12})\,\beta^* -\frac{1}{18r_0}\left(U''_{\rm nnn}+\frac{2}{r_0}U'_{\rm nnn}\right)\tilde{\beta}\,. \tag{31$'$}$$

Comparing with Eq. (26′), we find that in this model the many-body correction is about half of that in the previous case. One difficulty with this model is that the exact expression for A cannot be evaluated from the experimental value of $\tilde{C}_{44}-\tilde{C}_{12}$ along because of the occurrence of the term with f''. The correction factor A_1 deduced here differs from that given in Lundqvist,[15] who gets $\tilde{C}_{44}-\tilde{C}_{12}$ in place of $0.52(\tilde{C}_{44}-\tilde{C}_{12})$ in Eq. (31). The difference seems to be due to the fact that we have considered here many-body corrections to K from nearest-neighbor force constants only.

Basu and Roy[13] showed that the breathing-shell model effectively includes both three-body and four-body interactions. It is, however, not possible to write the many-body contribution to the lattice energy explicitly, since the effect occurs indirectly because of the breathing motion of the ions. The essential assumption of the breathing-shell model is that the lattice energy depends on ionic radii. The breathing motion is a new degree of freedom, which allows for the change of ionic radii for changes of ionic position. Usually the dependence on ionic radius is assumed to come from the overlap interaction.[15a] The van der Waals interaction also depends on ionic radii, through the polarizabilities of the ions. The significance of this dependence in the breathing-shell model has, however, not been discussed. Neglecting this effect, the expression for elastic constants are given by Basu and Roy.[13] The contribution to the compressibility from the breathing motion may be written in the form

$$1/\tilde{\beta}=-(\tilde{C}_{44}-\tilde{C}_{12})\,. \tag{32}$$

Since the breathing motion does not affect the long-wavelength optical vibrations, we have $A_1=1$. To get the factor A_2 we cannot use Eq. (22) directly as an explicit expression for the many-body contribution to cohesive energy, $U_{mb}=0$. Instead the repulsive energy in $U_{\rm nn}(r)$ depends on ionic radii which again owing to breathing motion are functions of r. Thus in the term $DU_{\rm nn}$ in Eq. (18) additional terms will come as a result of differentiation of ionic radii with respect to r. Using the adiabatic condition, we get ultimately from these terms the contribution to the compressibility due to breathing motion. Using Eq. (32), we get for the correction factor $A=A_1/A_2=1/A_2$

$$A=\frac{1}{A_2}=1+(\tilde{C}_{44}-\tilde{C}_{12})\tilde{\beta}-\frac{1}{18r_0}\left(U''_{\rm nnn}+\frac{2}{r_0}U'_{\rm nnn}\right)\tilde{\beta}\,. \tag{33}$$

Comparing with Eq. (26′), we find that the many-body correction for the breathing-shell model is the same as that from the many-body model of Sarkar and Sengupta.[16]

The three-body interaction in the exchange-charge model of Dick and Overhauser[11] is essentially the same as that in Lundqvist's model.[15] In both, the three-body interaction arises from an exchange effect and the difference arises from the different approximations used in the evaluation of the exchange integrals. Hence the correction factor A will be of the same form as in Eq. (31′), except for some difference in the numerical coefficient of the second term.

Lowndes and Martin[1] have considered the effect of a purely angle-dependent many-body interaction on the correction factor A. Such an interaction will evidently not contribute to the compressibility, because in a compressive strain the angles are not changed. But the contribution of this interaction to the nearest-neighbor force constant influences the optical vibration and contributes to A_1. According to the results given by Lowndes and Martin,[1] we get

$$\begin{aligned}1/\beta^*&=1/\beta^{*\prime}-(\tilde{C}_{44}-\tilde{C}_{12})\,,\\ 1/A_1&=1+(\tilde{C}_{44}-\tilde{C}_{12})\,.\end{aligned} \tag{34}$$

In this model U_{mb} is independent of r and from Eq. (22) we get

$$\frac{1}{A_2}=1-\frac{1}{18r_0}\left(U''_{\rm nnn}+\frac{2}{r_0}U'_{\rm nnn}\right)$$

and

$$A=\frac{A_1}{A_2}\simeq 1-(\tilde{C}_{44}-\tilde{C}_{12})-\frac{1}{18r_0}\left(U''_{\rm nnn}+\frac{2}{r_0}U'_{\rm nnn}\right)\,. \tag{34$'$}$$

Comparing with Eq. (26′), we find that the above correction due to the many-body interaction is of equal magnitude but of opposite sign. The reason for this difference lies in the fact that in this model no contribution from the many-body interaction comes from A_2. In fact, if we compare A_1 alone, we find that both the models give the same sign.

Thus we find that the correction due to the many-body interaction is the same as in the model of Sarkar and Sengupta.[16] In the model of Lundqvist[15] it is of the same sign but about half the magnitude. For a purely angle-dependent interaction,[1] on the other hand, it has the opposite sign. For the purpose of calculation we have used Eqs. (26′) and (34′) in exact form.

The results of the calculation of $S_2 = A\beta^*/\tilde{\beta}$ are given in Table I. The parameters of the overlap interaction are taken from Table X of Tosi.[17] The dielectric data for the calculation of β^* are taken from Ref. 1. S_2 is calculated using both the angle-dependent many-body interaction and the many-body interaction given in Ref. 16.

IV. DISCUSSION

The results given in Table I show that the value of S_2 is quite sensitive to the model of many-body interaction assumed. In 8 of the 15 crystals considered, $S_2 > 1$ in one of the two models of many-body interactions used. But for the remaining seven crystals, S_2 is either nearly equal to 1 or less than 1 in both models. The estimates of next-nearest-neighbor interactions are believed to be correct within a few percent. To give an idea of the differences, we may note that our estimate for LiF, based on Tosi's[17] Table X parameters, is -0.17 for $\tilde{\beta}/\tilde{\beta}_{nn}$. If Huggin's (see Born and Huang[8]) parameters, which are very different from those of Toshi, are used, the estimate is -0.22. It may be mentioned that according to the formula used by Lowndes and Martin,[1] the same correction term is -0.35. This large difference is partly due to the error in their formula and partly due to the fact that they have used calculated values of β_{nn} in their estimates of the correction term. Uncertainties in the estimate of the correction due to the many-body interaction, however, are much greater because of the difficulties in the determination of the values of $\tilde{C}_{44} - \tilde{C}_{12}$. In different sets of experimental results even the sign of this difference may be reversed. Thus, for example, $\tilde{C}_{12} - \tilde{C}_{44}$ for RbBr and RbI as given in Leibfried and Ludwig[14] are negative, while the values that we have used, based on later experiments, are positive. Even in these refined experiments, accuracy of measurement for C_{12} is not high and therefore considerable errors in $\tilde{C}_{44} - \tilde{C}_{12}$ are quite possible. In view of these uncertainties it is doubtful if a definite contradiction with the shell-model prediction can be concluded from the values of S_2 shown in Table I. Perhaps a more reasonable conclusion will be that the shell model is applicable for some crystals while the deformation-dipole model is better for the others.

When referring to the shell model, we have throughout this paper implied the conventional shell model which has been used in almost all the comparisons with experimental results. In this model the overlap force is assumed to act entirely through the shells. It is, however, possible to generalize the shell model by assuming that the short-range

TABLE I. Columns 2–5 give the experimental data used: harmonic value of nearest-neighbor distance $\tilde{r}_0$, compressibility ($\tilde{\beta}$), and difference $\tilde{C}_{44} - \tilde{C}_{12}$. Column 7 gives the values of the Szigeti constant S_2, assuming angle-dependent many-body interaction (Ref. 1), and column 8 gives S_2, if many-body interactions introduced by Sarkar and Sengupta (Ref. 16) are used. Values of β^* are calculated with the data given in Ref. 1. Column 6 gives the references of the elastic constants for the crystals in the corresponding row.

						$S_2 = A\beta^*/\tilde{\beta}$	
Crystal	$\tilde{r}_0$ (Å)	$\tilde{\beta}$ (10^{-12} cm^2/dyn)	β^* (10^{-12} cm^2/dyn)	$\tilde{C}_{44} - \tilde{C}_{12}$ (10^{-12} dyn/cm^2)	Ref.	From Eq. (34′)	From Eq. (26′)
LiF	1.990	0.960	1.147	−0.084	18	1.13	0.92
LiCl	2.538	2.884	3.406	0.053	19	0.72	1.03
LiBr	2.713	3.759	4.634	0.058	20	0.63	1.06
NaF	2.295	1.897	1.825	0.076	21	0.72	0.96
NaCl	2.790	3.614	3.757	0.031	14	0.83	1.04
NaBr	2.951	4.348	4.727	0.013	21	0.88	1.00
NaI	3.198	5.504	6.414	0.002	22	0.95	0.98
KF	2.637	2.772	2.812	0.001	23	0.87	0.87
KCl	3.108	4.785	4.835	0.012	14	0.90	1.01
KBr	3.258	5.577	5.629	0.004	24	0.94	0.99
KI	3.484	7.559	6.943	0.013	25	0.79	0.96
RbF	2.788	3.145	3.393	−0.035	14	0.96	0.71
RbCl	3.239	4.902	5.338	−0.026	19	1.22	0.90
RbBr	3.408	6.154	6.352	−0.003	21	1.03	0.98
RbI	3.625	7.519	7.669	−0.007	21	1.06	0.95

overlap interaction between two ions acts through core-core (D), shell-shell (S), and core-shell [$F(12) = F(21) = F$] interactions. If we restrict ourselves to nearest-neighbor interactions and the corresponding spring constants are written K_D, K_S, and K_F, respectively, then it can be shown that[26]

$$S_2 = \left(1 - \frac{K'^2(K_1 + K_2 + 2K_F)}{K(K_1 + K_F)(K_2 + K_F) + KK_S(K_1 + K_2 + 2K_F)}\right)^{-1}, \tag{35}$$

where

$$K' = K_S + K_F \ , \ K = K_D + K_S + 2K_F$$

and K_1 and K_2 are the core-shell spring constants of the individual ions.

It is easily seen that for the conventional shell model $K_D = K_F = 0$ and $K = K' = K_S$, and S_2 in Eq. (28) reduces to the value given in Eq. (11). If we assume $K_S = K_F = 0$, then $K' = 0$ and $S_2 = 1$. In this case the short-range polarization is completely neglected and only the electrical polarizability is taken account of. If only K_S is put equal to zero, i.e., the shell-shell interaction is neglected, then the model takes account of the short-range polarization. But S_2 remains greater than 1. Thus the generalized shell model in this approximation is similar but not identical to the deformation-dipole model. As far as the long-wavelength optical vibrations are concerned, the essential difference between the two models is that in the deformation-dipole model it is assumed that the ionic spring constant K is not effectively changed by the development of deformation dipole. In the shell model, on the other hand, this spring constant is effectively reduced in magnitude.

As has been pointed out earlier, in our definition of the constants S_1 and S_2 all experimental quantities refer to the harmonic values, so that no effect of anharmonicity is included in the Szigeti constants. In computing S_2 values of Table I, we have used the harmonic values of r_0 and β, but zero-degree values of ϵ_0, ϵ_∞, and ω_0. The effect of zero-degree anharmonicity on these quantities is quite small. For example, from the measurement of Lowndes and Martin[1] we find that for NaCl, the difference between the harmonic and the zero-degree value of ϵ_0 is only 0.8% and for KCl it is 0.2%. The effect on ω_0 can be easily estimated from the change in the spring constant K due to the difference in the harmonic and zero-degree values of r_0. It is found that for KF the change in ω_0 is about 1%. This is quite negligible compared to the effect we are discussing.

It is particularly interesting to note that in none of the cases is S_2 found to be definitely less than 1 in both the models of many-body interactions. The worst case is that of KF, where $S_2 = 0.87$. This is important in view of the fact that none of the models of ionic crystals predicts a value of $S_2 < 1$. The present analysis shows that it is not possible to explain the properties of all the crystals on a single model and a single type of many-body interaction. The nature of the model and the type of many-body interaction will vary from crystal to crystal.

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