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Extended three-body-force shell-model dynamics of sodium-halide crystals

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An extended three-body-force shell model has been developed for the lattice dynamics of ionic crystals by incorporating the effect of three-body and second-neighbor forces in the framework of the shell model with both ions polarizable. The versatility of the model has been tested by carrying out a qualitative analysis of the elastic and dielectric behavior of ionic crystals of rocksalt structure in general and a quantitative analysis of the phonon dispersion in sodium halides in particular. The model has been found to possess some remarkable features and describe more satisfactorily the dispersion of phonons in sodium halides as compared to those revealed by the original three-body-force shell model and other models.

I. INTRODUCTION

During the last decade some useful phenomenological models[1–4] have been developed for the lattice dynamics of ionic crystals. These models generally employ the electron-shell deformation effects in terms of effective many-body interactions[5] in the framework of the rigid-shell model[6] (RSM) to explain the Cauchy violation and dynamical properties. Parallel to this, various microscopic models[7–9] have been developed for the study of general properties of phonons. However, one difficulty common to all of them is that their mathematical equations are too complicated and unless drastic approximations are made numerical calculations become impossible. In contrast, the formulations of other models[1–4] are relatively simple and easily adaptable for the computations. Consequently, the most extensively used amongst them are the breathing-shell model[1] and three-body-force shell model[4] (TSM). The basis for the introduction of the radial expansion rate of the shells as an additional degree of freedom in the former is, however, not clearly understood. Also, it takes account of the Cauchy violation only approximately, while the nature of three-body forces is well known and their inclusion in TSM is based on Löwdin-Lundqvist microscopic theory[10,11] which is considered to be the most appealing and realistic approach to represent the interatomic interactions and explain the Cauchy violation in ionic crystals. In addition, the TSM framework is almost identical[12] to the microscopic model of Sinha.[8] Thus, it may be regarded as ingenious blending of microscopic considerations in the phenomenological scheme of RSM. Furthermore, the TSM has described satisfactorily the lattice dynamics of almost all the ionic crystals, namely, the monovalent metal halides[12–15] and divalent metal oxides.[16]

Despite several remarkable successes outlined above, the TSM suffers from some limitations which have recently been pointed out by Singh and Gupta.[17] These limitations are subject to an inconsistency which is involved in the definition of ionic, core, and shell charges and leads to the incorrect expressions for the electrical and mechanical polarizabilities. Also, the short-range interactions are limited only to the first neighbors while the same between second neighbors contribute significantly in most of the cases. These deficiencies clearly indicate the necessity for further refinement of TSM for better description of interatomic forces and lattice dynamics of ionic solids.

The need for such refinements is also obvious from the remark of Singh and Verma[12] that the discrepancies observed in the prediction of dispersion curves of sodium halides are so significant at some points that TSM deserves to be refined further. One possible direction of improvement suggested by them[12] is the inclusion of second-neighbor short-range interactions which will enable TSM to establish closer identity with Sinha's microscopic model and reduce the largest deviation appearing in the longitudinal optical branch along the (q, q, q) direction, especially in the case of NaI.

The chief object of this paper is to report the corrected and extended framework of TSM and investigate the applicability of the resultant model designated as extended TSM (ETSM) to describe the lattice dynamics of sodium halides. The efforts devoted in this regard have revealed several remarkable features outlined in the following:

(i) The off-diagonal elements of the dynamical matrix corresponding to ETSM contain a completely new and significant term besides minor modifications introduced in various other quantities involved in their expressions as compared to the original TSM.[18]

(ii) The zone-center optical vibration frequencies involving three-body-force parameters while satisfying the Lyddane-Sachs-Teller (LST) relations introduce important modifications in other microscopic relations like the Clausius-Mossotti (CM), Lorentz-Lorenz (LL), Szigeti,[19] and Ruffa[20] relations. These derivations are of great academic interest and importance since the relations clearly demonstrate the three-body-force effects and correlate the optical and mechanical properties of solids through interatomic forces and crystal polarizabilities. The numerical effect of these modifications seems to be quite significant in the case of solids with large Cauchy discrepancy. It is worth mentioning that the analytical expressions of these relations although apparently different from those reported by Verma and Agrawal[21] ultimately lead to similar conclusions.

(iii) The ETSM framework seems to be quite capable and adequate for the description of phonons and interatomic interactions in ionic crystals.

The latter fact is self-evident from the consequences explored from ETSM to predict the measured phonon dispersion data which provide the most dependable test of any model since the eigenvectors of the normal modes are not well known. The analysis carried out here for sodium halides has yielded excellent agreement between theoretical and experimental dispersion curves in which much information referring to optical, dielectric, elastic and thermodynamic properties of crystals is embodied. The motivation for the selection of sodium-halide crystals has been the availability of such curves for all of them (NaF,[22] NaCl,[23] NaBr,[24] and[25] NaI) and the continued interest in them since the last few decades. Further work on the features of their infrared absorption and Raman scattering spectra and Debye-temperature variations even though they provide a relatively less sensitive test, is in progress and expected to reveal their interpretation with almost the same success as that on the phonons.

A brief theory of ETSM with its noteworthy features has been described in Sec. II. The results computed for the sodium halides with this model have been presented in Sec. III and discussed in Sec. IV.

II. THEORY OF EXTENDED TSM (ETSM)

A. General formulations

The theory of ETSM basically includes the effect of three-body forces and short-range repulsion effective up to second neighbors in the framework of both ions polarizable shell model. The former effect has been included on the basis of Löwdin-Lundqvist microscopic theory of overlap of adjacent ions in crystals. The general formalism of ETSM can be derived from the crystal potential energy expressed as (Lundqvist[11])

$$U(r)=\frac{1}{2}\sum_{lk}\sum_{\substack{l'k'\\(lk\neq l'k')}}\frac{Z_kZ_{k'}e^2}{|r(lk;l'k'|}+\frac{1}{2}\sum_{lk}\sum_{l'k'}\Phi(|r(lk;l'k')|)+\sum_{lk}\sum_{l'k'}\sum_{\substack{l''k''\\(lk\neq l'k'\neq l''k'')}}Z_k e f_k(r(lk;l''k''))\frac{Z_{k'}e}{|r(lk;l'k'|}\ , \qquad (1)$$

where the first two terms represent the usual two-body long-range Coulomb and short-range repulsive interaction potentials. The last term contains interactions of three-body character (Löwdin,[10] Lundqvist[11]) which can be calculated as if a charge $\Delta q=\pm Z_k e f(r)$ is transferred to the ion (lk) from the neighboring ion $(l''k'')$ due to the overlap of electron shells and this in turn interacts with $Z_{k'}e$ at $(l'k')$ via Coulomb's law. Here $f(r)$ is a function proportional to the square of the overlap integrals[10,11] between two neighboring ions and dependent on the separation (r) between them. As usual, it can be shown that three-body forces of Eq. (1) modify the long-range Coulomb and short-range repulsive parts and introduce an explicitly three-body term to the dynamical matrix of ionic crystals of rocksalt structure.

Based on Eq. (1) and postulating the overlap repulsion effective upto the second neighbors and following closely the method of Woods, Cochran, and Brockhouse,[6] the equations of motion of ETSM can be written

$$\omega^2 MU=(R+Z_mC'Z_m)U+(T+Z_mC'Y_m)W, \qquad (2)$$

$$0=(T^T+Y_mC'Z_m)U+(S+K+Y_mC'Y_m)W, \qquad (3)$$

where $Z_m e=Z[1+6f(r_0)]e$ denotes the effective ionic charge (Cochran[26]) modified from its original values Ze (Woods *et al.*[6]). In view of the smallness of three-body force parameter f_0 $[=f(r_0)]$, we can write $Z_m=\pm Z(1+12f_0)^{1/2}$ since $(1+6f_0)^2$ can be approximated as $(1+12f_0)$. Consequently, the original core and shell charges (X, Y) will be modified to (X_m, Y_m) given by $Z_m=X_m+Y_m=xZ_m+yZ_m$ with the reduced charges (x, y) such that $x+y=\pm 1$. This correction has led to the following expressions for the electrical and mechanical polarizabilities:

$$\alpha_i=\frac{(Y_{mi}e)^2}{k_i+(R_{ii})_{q\to 0}},\quad d_i=-\frac{Y_{mi}(R_{ii})_{q\to 0}}{k_i+(R_{ii})_{q\to 0}},\quad i=1,2, \qquad (4)$$

which have been modified significantly as compared to those derived from the original TSM.[12,18]

In Eqs. (2) and (3) R, T, and S are (6×6) matrices that represent the short-range "atom-atom," "atom-dipole," and "dipole-dipole" interaction matrices, respectively. In order to reduce the number of parameters they have been treated equal ($R = T = S$) by allowing the short-range forces to act only through the shells. The expressions required to evaluate R have already been derived by Cowley.[27] C' represents the modified long-range interaction matrix given by

$$C' = C + Z_m^{-2} Z r_0 f_0' V , \tag{5}$$

where C and V are the Coulomb and three-body interaction matrices already defined and evaluated by Kellermann[28] and Verma and Singh,[4] respectively.

It seems appropriate at this juncture to point out the feature which merits attention and occurs mainly due to the difference in the representation of C' in the present form and that of Verma and Singh[4] (see also Verma and Agrawal[29]) as

$$C' = Z_m^2 C + V . \tag{6}$$

This representation seems questionable since as such it allows Z_m to attain the power 4 instead of 2 in the equations of motion [Eqs. (2) and (3)]. The above difference also leads to the differences appearing throughout in various formulas describing optical behavior of ionic crystals to be described a little later. However, this inadvertent error could not be detected in numerical analysis carried out by Verma and Agrawal[29] since in their computer program Z_m^2 has been multiplied only with C and not with V.

The elimination of W from Eqs. (2) and (3) leads to the usual secular determinant

$$|D - m_a \omega^2| = 0 , \tag{7}$$

with its (6×6) dynamical matrix

$$\begin{aligned} D(q) = {} & (R + Z_m C' Z_m) - (T + Z_m C' Y_m) \\ & \times (S + K + Y_m C' Y_m)^{-1} (T^T + Y_m C' Z_m) . \end{aligned} \tag{8}$$

This matrix along symmetry directions reduces to (2×2) with elements $D_{11}^{\alpha\beta}(q)$, $D_{22}^{\alpha\beta}(q)$, and $D_{12}^{\alpha\beta}(q) = D_{21}^{\alpha\beta}(q)$. The expressions for them derived recently by Singh and Gupta[17] show that the off-diagonal elements $D_{12}^{\alpha\beta}(q)$ contain a completely new term which has appreciable contribution of about (5–10)% when the shell charges are treated unequal and contributes zero for equal shell charge considerations. In order to calculate the eigenvalues (ω) for any general (or symmetry) direction the solution of Eq. (7) will require the knowledge of the parameters involved in the dynamical matrix. These parameters are generally calculated by relating them with macroscopic data like elastic, optic, and dielectric constants. The derivation of these relations can be carried out by examining the long-wavelength aspects of ETSM.

B. Long-wavelength aspect of ETSM

In order to investigate the long-wavelength characteristics of ETSM, we will follow closely the method of long waves as adapted to the shell model by Cowley[27]; to save space, the arguments parallel to those presented there will not be generally repeated.

1. Long-wave elastic behavior

The expressions for the elastic constants can be derived from the dynamical matrix of ETSM and obtained to be

$$\begin{aligned} C_{11} = {} & (e^2/4r_0^4)[-5.112 Z_m^2 + A_{12} + \tfrac{1}{2}(A_{11} + A_{22}) \\ & + \tfrac{1}{2}(B_{11} + B_{22}) + 9.3204 Z r_0 f_0'] , \end{aligned} \tag{9}$$

$$\begin{aligned} C_{12} = {} & (e^2/4r_0^4)[0.226 Z_m^2 - B_{12} + \tfrac{1}{4}(A_{11} + A_{22}) \\ & - \tfrac{5}{4}(B_{11} + B_{22}) + 9.3204 Z r_0 f_0'] , \end{aligned} \tag{10}$$

$$\begin{aligned} C_{44} = {} & (e^2/4r_0^4)[2.556 Z_m^2 + B_{12} + \tfrac{1}{4}(A_{11} + 3B_{11}) \\ & + \tfrac{1}{4}(A_{22} + 3B_{22})] . \end{aligned} \tag{11}$$

Where A_{ij} and B_{ij} are the radial and tangential force constants between nearest- ($i \neq j$) and next-nearest-neighbor ($i = j$) ions defined as

$$\begin{aligned} \frac{e^2}{2V}(A_{ij}) &= \left(\frac{d^2 \Phi_{ij}^R(r)}{dr^2}\right)_{r=r_0} , \\ \frac{e^2}{2V}(B_{ij}) &= -\left(\frac{1}{r}\frac{d}{dr}\,\Phi_{ij}^R(r)\right)_{r=r_0} , \\ \frac{e^2}{2V}(A_{ii}) &= \left(\frac{d^2 \Phi_{ii}^R(r)}{dr^2}\right)_{r=r_0\sqrt{2}} , \\ \frac{e^2}{2V}(B_{ii}) &= -\left(\frac{1}{r}\frac{d}{dr}\,\Phi_{ii}^R(r)\right)_{r=r_0\sqrt{2}} . \end{aligned} \tag{12}$$

Introducing these notations in Eq. (1) and imposing it to the equilibrium condition

$$\left(\frac{d}{dr}\,U(r)\right)_{r=r_0} = 0 ,$$

we get

$$B_{11} + B_{22} + B_{12} = -1.165 Z_m^2 . \tag{13}$$

In view of this relation, the above elastic constants lead to the Cauchy violation

$$C_{12} - C_{44} = (e^2/4r_0^4)(9.3204 Z r_0 f_0') \tag{14}$$

and the compressibility

$$\begin{aligned} 1/\beta = \tfrac{1}{3}(C_{11} + 2C_{12}) = {} & R_0/6r_0 + (e^2/12r_0^4)(A_{11} + 2B_{11} \\ & + A_{22} + 2B_{22}) + (e^2/12r_0^4)(27.9612 Z r_0 f_0') . \end{aligned} \tag{15}$$

The first term is usual Born-model contribution, the middle one is due to the second-neighbor short-range interactions and the last one is purely three-body interaction term.

2. *Long-wave optical behavior*

In order to demonstrate qualitatively the capabilities of ETSM to describe the optical behavior of solids certain well-known macroscopic relations have been derived in this section. These relations have although been derived (Born and Huang[30]) earlier but by neglecting the effect of overlap of electron shells of the ions.

a. Modified C-M and L-L relations. The expression for the effective field (E_{eff}) polarizing the ion can be derived from the crystal energy given by Eq. (1) and written (Kellermann[28])

$$E_{\text{eff}} = E_{\text{ext}} + \tfrac{4}{3}\pi P + \lambda P \ , \tag{16}$$

where E_{ext} is the external field. The second and last terms are contributed by the long-range Coulomb and three-body interactions, respectively. P represents the polarization due to the ions with effective charge $\pm Z_m e$ and the abbreviation λ stands for

$$\lambda = 16\pi Z r_0 f_0' / 3Z_m^2 \, . \tag{17}$$

Now, employing the polarizability relations

$$P = (\alpha/V) E_{\text{eff}} \quad \text{and} \quad P/E = (\epsilon - 1)/4\pi \, , \tag{18}$$

one could easily obtain from Eq. (16) the following modified LL and CM relations:

$$\frac{(\frac{4}{3}\pi + \lambda)\alpha/V}{1 + (\lambda\alpha/V)} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}$$

and

$$\frac{(\frac{4}{3}\pi + \lambda)(\alpha + \alpha_I)/V}{1 + \lambda[(\alpha + \alpha_I)/V]} = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \ . \tag{19}$$

Here, α and α_I correspond to the electronic and ionic polarizabilities, respectively.

b. Lyddane-Sachs-Teller(LST) relations. Following usual procedure, the long-wave optical vibration frequencies (ω_{L}, ω_{T}) can be written

$$\mu\omega_{\text{L}}^2 = R_0' + (8\pi/3V)[(Z'e)^2/f_L](1 + 6Z_m^{-2} Z r_0 f_0') \, , \tag{20}$$

$$\mu\omega_{\text{T}}^2 = R_0' - (4\pi/3V)(Z'e)^2/f_{\text{T}} \, , \tag{21}$$

which by means of simple algebraic manipulations can be recasted to the most symmetrical form

$$\mu\omega_{\text{L}}^2 = R_0'[1 + (\tfrac{8}{3}\pi + 3\lambda)(\alpha + \alpha_I)/V] \times [1 + (\tfrac{8}{3}\pi + 3\lambda)\alpha/V]^{-1} \, , \tag{22}$$

$$\mu\omega_{\text{T}}^2 = R_0'[1 - \tfrac{4}{3}\pi(\alpha + \alpha_I)/V](1 - \tfrac{4}{3}\pi\alpha/V)^{-1} \, , \tag{23}$$

where

$$R_0' = R_0 - e^2(d_1^2/\alpha_1 + d_2^2/\alpha_2) = (Z'e)^2/\alpha_I \, ,$$

$$Z' = Z_m + d_1 - d_2 \, ,$$

$$f_{\text{L}} = 1 + (\tfrac{8}{3}\pi + 3\lambda)\alpha/V \, , \quad f_{\text{T}} = 1 - \tfrac{4}{3}\pi\alpha/V \, .$$

The elimination of α and α_I from Eqs. (22) and (23) with the help of L-L and C-M relations (19) will lead to the following LST relations:

$$(\omega_{\text{L}}/\omega_{\text{T}})^2_{q\to 0} = \epsilon_0/\epsilon_\infty \, , \tag{24}$$

$$\omega_S^2 = \omega_{\text{T}}^2[(\epsilon_0 + 2)/(\epsilon_\infty + 2)] \, . \tag{25}$$

Here, ω_S is the triply degenerate infrared frequency given by

$$\mu\omega_S^2 = R_0'[1 + (\lambda/V)(\alpha + \alpha_I)](1 + \lambda\alpha/V)^{-1} \, , \tag{26}$$

and can be derived from Eq. (16). The static- and high-frequency dielectric constants in above relations read as

$$\epsilon_0 = [1 + (\tfrac{8}{3}\pi + 3\lambda)(\alpha + \alpha_I)/V] \times [1 - \tfrac{4}{3}\pi(\alpha + \alpha_I)/V]^{-1} \, , \tag{27}$$

$$\epsilon_\infty = [1 + (\tfrac{8}{3}\pi + 3\lambda)\alpha/V](1 - \tfrac{4}{3}\pi\alpha/V)^{-1} = f_{\text{L}}/f_{\text{T}} \, . \tag{28}$$

c. Szigeti relations. Using Eqs. (20) and (21), the splitting of optical phonons can be obtained as

$$\mu(\omega_{\text{L}}^2 - \omega_{\text{T}}^2) = [3(Z'e)^2/Vf_{\text{L}}f_{\text{T}}](\tfrac{4}{3}\pi + \lambda) \, . \tag{29}$$

Alternatively, it can also be expressed as

$$\mu(\omega_{\text{L}}^2 - \omega_{\text{T}}^2) = [4\pi(Z_m + d_1 - d_2)^2 e^2/Vf_{\text{L}}f_{\text{T}}] \times (1 + 12f_0 + 4Zr_0 f_0')(1 + 12f_0)^{-1} \, . \tag{30}$$

This splitting as compared to one derived from the original TSM

$$\mu(\omega_{\text{L}}^2 - \omega_{\text{T}}^2) = [4\pi(Z_m + d_1 - d_2)^2 e^2/Vf_{\text{L}}f_{\text{T}}] \times (1 + 12f_0 + 4Zr_0 f_0') \tag{31}$$

qualitatively differs by a factor $(1 + 12f_0)^{-1}$.

Now, substituting the LST relation (24) into Eq. (29) we get,

$$\mu\omega_{\text{T}}^2(\epsilon_0/\epsilon_\infty - 1) = [3(Z'e)^2/Vf_{\text{T}}^2](f_{\text{T}}/f_{\text{L}})(\tfrac{4}{3}\pi + \lambda) \, . \tag{32}$$

Since $\epsilon_\infty = f_{\text{L}}/f_{\text{T}}$ from Eq. (28) and

$$(\epsilon_\infty + 2)^2 = (f_{\text{L}} + 2f_{\text{T}})^2/f_{\text{T}}^2 = (9/f_{\text{T}}^2)(1 + \lambda\alpha/V)^2 \, .$$

Therefore, the Eq. (32) reduces to

$$\mu\omega_{\text{T}}^2 = \frac{(Z'e)^2(\epsilon_\infty + 2)^2}{3V(\epsilon_0 - \epsilon_\infty)} \frac{(\frac{4}{3}\pi + \lambda)}{(1 + \lambda\alpha/V)^2} \, , \qquad \omega_{\text{T}}^2 = [4\pi(\epsilon_\infty + 2)^2/9\mu V(\epsilon_0 - \epsilon_\infty)]\, e^{*2} \ . \tag{33}$$

This represents the first Szigeti relation with modified Szigeti effective charge given by

$$e^* = [Z'(1 + 3\lambda/4\pi)^{1/2}(1 + \lambda\alpha/V)^{-1}]e \, . \tag{34}$$

This effective charge is contributed by both the three-body forces arising from the electron shell deformations and the shell distortions due to overlap of neighboring ions.

By employing simple manipulations in the expressions of β given by Eq. (15), the second modified Szigeti relation can be obtained as

$$(\beta^*/\beta)=(\beta^*/\beta)_S\{1+(e^2/R_0V)[(A_{11}+2B_{11}+A_{22}+2B_{22})+27.9612Zr_0f_0']\}, \quad (35)$$

where $(\beta^*/\beta)_S$ represents the original Szigeti relation given by

$$(\beta^*/\beta)_S=[1-(e^2/R_0)(d_1^2/\alpha_1+d_2^2/\alpha_2)^{-1}]. \quad (36)$$

The modification introduced in the second Szigeti relation (35) is evident from the last two terms which are contributed by the second-neighbor and three-body interactions.

d. Modified Ruffa's equation. The ions experience loosening and tightening effects when they enter the crystal from free state due to the nature of the Madelung potential at the cation and anion sites according to Ruffa's theory.[19] In ETSM, since the usual Madelung energy has been modified by a factor $Z_m=\pm Z(1+12f_0)^{1/2}$, therefore the modified Ruffa's equations will be given by

$$\frac{\alpha_c^+}{\alpha_f^+}=\frac{\bar{E}_1^2}{(\bar{E}_1-Z_me\phi_m)^2}, \quad R_c^+=\frac{nc}{\bar{E}_2-Z_me\phi_m}, \quad (37)$$

where α_c^+ and α_f^+ represent the cation polarizabilities in crystalline and free state of ions, $\bar{E}_1$ and $\bar{E}_2$ are mean excitation energies which can be determined using the values of polarizabilities (Pauling[31]) and ionic radii (Pauling[32]), $\phi_m=-e^2\alpha_m/r_0$ is the Madlung energy, $c=h^2/8\pi^2m$, and n is the number of electrons in the ion.

It is evident from the above ETSM description of dielectric behavior that three-body forces introduce important modifications in L-L, C-M, Szigeti, and Ruffa relations and leave the LST relations unaffected. A similar conclusion has also been drawn by Verma and Agrawal[21] but their expressions slightly differ from those derived by us to the basic difference in the representation of C' as pointed out earlier [see Eqs. (5) and (6)].

e. Strategy for parameter determination. The ETSM theory described above contains 12 parameters: A_{12}, B_{12}, A_{11}, B_{11}, A_{22}, B_{22}, d_1, d_2, α_1, α_2, Z_m, and r_0f_0'. The expressions connecting them with macroscopic quantities: C_{11}, C_{12}, C_{44}, ω_L, ω_T, r_0, ϵ_0, and ϵ_∞, are just sufficient to determine only 8 parameters. The problem of evaluating the rest 4 parameters has been solved by deriving the expressions for the known frequencies corresponding to the L point (0.5, 0.5, 0.5) given below:

$$m_1\omega_{\mathrm{LA}}^2(L)=R_0+(e^2/V)(2A_{11}+B_{11})-e^2d_1^2/\alpha_1+(e^2/V)C_{1\mathrm{L}}'(Z_m+d_1)^2[1+(\alpha_1/V)C_{1\mathrm{L}}']^{-1}, \quad (38)$$

$$m_2\omega_{\mathrm{LO}}^2(L)=R_0+(e^2/V)(2A_{22}+B_{22})-e^2d_2^2/\alpha_2+(e^2/V)C_{1\mathrm{L}}'(Z_m-d_2)^2[1+(\alpha_2/V)C_{1\mathrm{L}}']^{-1}, \quad (39)$$

$$m_1\omega_{\mathrm{TA}}^2(L)=R_0+(e^2/2V)(A_{11}+5B_{11})-e^2d_1^2/\alpha_1+(e^2/V)C_{1\mathrm{T}}'(Z_m+d_1)^2[1+(\alpha_1/V)C_{\mathrm{T}}']^{-1}, \quad (40)$$

$$m_2\omega_{\mathrm{TO}}^2(L)=R_0+(e^2/2V)(A_{22}+5B_{22})-e^2d_2^2/\alpha_2+(e^2/V)C_{1\mathrm{T}}'(Z_m-d_2)^2[1+(\alpha_2/V)C_{1\mathrm{T}}']^{-1}, \quad (41)$$

where

$$R_0=(e^2/V)(A_{12}+2B_{12}),$$

$$C_{1\mathrm{L}}'=-[(C_{1xx}+2C_{1xy})+(V_{1xx}+2V_{1xy})Z_m^{-2}Zr_0f_0']_{0.5,0.5,0.5},$$

$$C_{1\mathrm{T}}'=-[(C_{1xx}-C_{1xy})+(V_{1xx}-V_{1xy})Z_m^{-2}Zr_0f_0']_{0.5,0.5,0.5}.$$

In view of the scarcity of useful equations and the necessity for determination of crystal polarizabilities (α_1, α_2), we have employed a reasonable assumption according to which the ratio of the electronic polarizabilities of free ions is equal to that of the ions in crystals, i.e., $(\alpha_1/\alpha_2)^f=(\alpha_1/\alpha_2)^c$. The justification for this assumption has been given by Carabatos and Prevot.[33] The use of such an assumption became essential in our case since the four quantities (ω_L, ω_T, ϵ_0, ϵ_∞) are equivalent to only three independent quantities in view of LST relation. The knowledge of the parameters thus obtained enables one to compute the phonon spectra and associated phsycial properties of the crystals with ETSM.

III. COMPUTATIONS AND RESULTS

A detailed theoretical treatment of ETSM presented in the preceding section shows qualitatively the role of second-neighbor and three-body forces to describe the dynamical and dielectric properties of ionic crystals. This analysis, however, alone cannot lead to a definite conclusion about their roles unless the effects are thoroughly investigated quantitatively. Thus, in order to test the versatility of the model completely it has been applied to compute the dispersion curves of sodium halides for phonons propagating along principal symmetry directions $\vec{\Delta}$, $\vec{\epsilon}$, and $\vec{\Lambda}$ of the crystals. These calculations have been performed using the model parameters listed in Table I and obtained with the macroscopic data given in Table II and the formulation described in Sec. II. It may also be pointed out that in order to achieve satisfactory agreement and reasonable values of the parameters, the polarizability ratio in case of NaBr and NaI have been taken from the fitted values re-

Table I. Model parameters for sodium halides.

	Values			
Parameters	NaF	NaCl	NaBr	NaI
A_{12}	10.924 79	11.645 84	12.554 19	11.745 69
B_{12}	−1.061 56	−1.255 81	−1.466 00	−0.987 66
A_{11}	−1.471 89	−0.945 40	−1.080 06	−2.177 98
B_{11}	0.069 13	0.167 66	0.120 92	0.323 77
A_{22}	1.371 63	1.027 67	1.309 09	1.997 58
B_{22}	−0.169 39	−0.085 39	0.108 11	−0.504 17
α_1	0.485 23	0.616 30	1.550 00	1.921 38
α_2	0.761 15	2.580 00	3.600 00	4.211 51
d_1	0.010 07	0.002 88	0.004 80	0.022 14
d_2	0.208 51	0.267 63	0.267 29	0.365 99
Z_m	0.998 63	1.003 66	1.030 42	1.001 31
$r_0 f_0'$	−0.019 66	−0.015 06	−0.078 31	−0.003 50

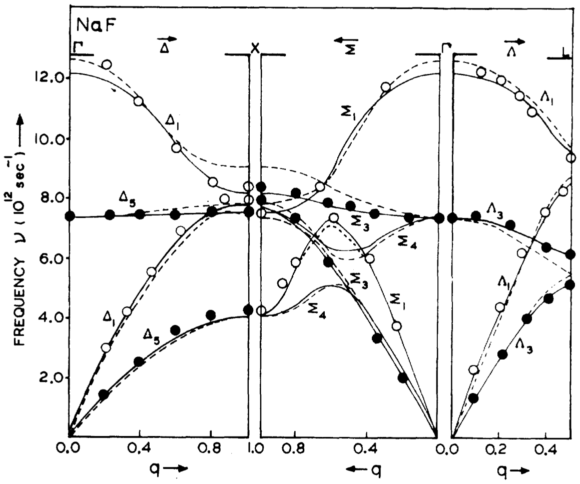

FIG. 1. Dispersion curves for NaF. Theoretical curves (solid line) ETSM, (dashed line) DSM (Ref. 2). Experimental points (Ref. 22) (○—longitudinal, ●—transverse).

ported by Reid *et al.*[24] and Woods *et al.*,[25] respectively.

The phonon dispersion curves derived from ETSM and those determined from the neutron spectrometry for NaF, NaCl, NaBr, and NaI have been displayed in Figs. 1–4, respectively. The dispersion curves obtained by Melvin *et al.*[2] using the deformable-shell model[2] (DSM) have also been shown in the same figures. This will enable us to judge the relative merit of ETSM over DSM by visual comparison.

IV. DISCUSSIONS

A glance at the dispersion curves given in the Figs. 1–4 reveals excellent agreement between theoretical and experimental results for almost all the sodium halides. As compared to our results, the DSM results show considerably large deviations from the experimental ones especially towards the higher-wave-vector region for the optic (Δ_1, Δ_5, Σ_1, Σ_3, Λ_1, and Λ_3) and acoustic (Σ_4 and Λ_3) branches in almost all the materials under consideration. The maximum deviations are generally (8–12)% with exceptionally high up to 15%

Table II. Input data for sodium halides.

Constants	NaF values	Ref.	NaCl values	Ref.	NaBr values	Ref.	NaI values	Ref.
$C_{11}(10^{11}\ \mathrm{dyn\,cm^{-2}})$	9.710	36	5.838	39	4.800	42	3.590	2
$C_{12}(10^{11}\ \mathrm{dyn\,cm^{-2}})$	2.430	36	1.194	39	0.542	b	0.750	2
$C_{44}(10^{11}\ \mathrm{dyn\,cm^{-2}})$	2.800	36	1.327	39	1.070	42	0.768	2
$\nu_L(\Gamma)\ (10^{12}\ \mathrm{sec^{-1}})$	12.176	a	7.830	23	6.220	24	5.170	25
$\nu_T(\Gamma)\ (10^{12}\ \mathrm{sec^{-1}})$	7.385	22	5.172	23	4.040	24	3.600	25
$\nu_{Lo}(L)\ (10^{12}\ \mathrm{sec^{-1}})$	9.980	22	6.907	23	5.830	24	5.270	25
$\nu_{To}(L)\ (10^{12}\ \mathrm{sec^{-1}})$	6.190	22	4.168	23	3.810	24	3.500	25
$\nu_{LA}(L)\ (10^{12}\ \mathrm{sec^{-1}})$	8.543	22	5.332	23	3.180	24	2.360	25
$\nu_{TA}(L)\ (10^{12}\ \mathrm{sec^{-1}})$	5.145	22	3.613	23	2.160	24	1.530	25
$\left(\frac{\alpha_1}{\alpha_2}\right)^f$	$\frac{0.408}{0.640}$	37	$\frac{0.6163}{2.58}$	40	$\frac{1.56}{3.64}$	24	$\frac{1.98}{4.34}$	25
ϵ_∞	1.739	37	2.25	30	2.438	c	2.91	25
$r_0(10^{-8}\ \mathrm{cm})$	2.312	38	2.7935	41	2.987	38	3.199	43

[a] Calculated from LST relation using $\epsilon_0 = 4.73$ (Ref. 44).
[b] Calculated from β relation using $\beta = 5.1 \times 10^{-12}\ \mathrm{dyn^{-1}\,cm^2}$ (Ref. 45).
[c] Calculated from LST relation using $\epsilon_0 = 5.78$ (Ref. 44).

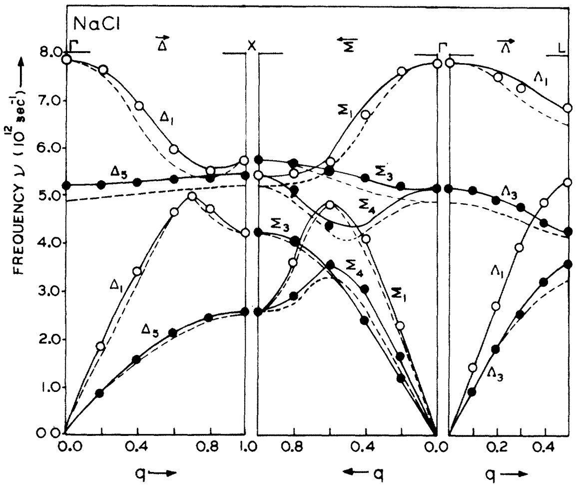

FIG. 2. Dispersion curves for NaCl. Theoretical curves (solid line) ETSM, (dashed line) DSM (Ref. 2). Experimental points (Ref. 23) (o—longitudinal, ●—transverse).

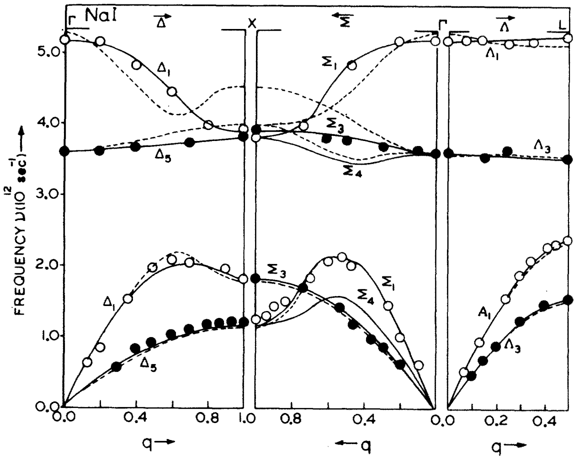

FIG. 4. Dispersion curves for NaI. Theoretical curves (solid line) ETSM, (dashed line) DSM (Ref. 2). Experimental points (Ref. 25) (o—longitudinal, ●—transverse).

for Δ_1(Lo) and ϵ_3(TO) branches in case of NaI. In addition to these deviations, the DSM results possess some unusual features of sudden rise of branch near the zone-boundary point (X) in all the cases. Such features are, however, not exhibited by experimental results although they have been noticed from the breathing-shell model[1] (BSM) results particularly for NaCl.[34] This similarity between BSM and DSM is not unexpected because both of them account for the radial deformations almost identically. The absence of such unusual features and large deviations in the ETSM description of dispersion curves make it evident that the representation of electron shell deformations in terms of three-body forces is better than those of radial deformations as pointed out earlier in the introduction.

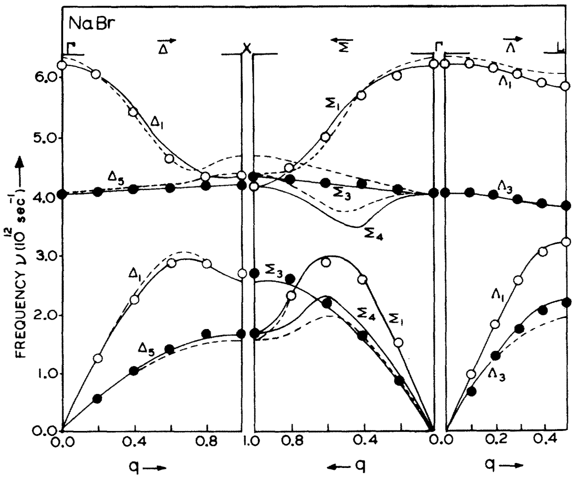

FIG. 3. Dispersion curves for NaBr. Theoretical curves (solid line) ETSM, (dashed line) DSM (Ref. 2). Experimental points (Ref. 24) (o—longitudinal, ●—transverse).

The literature available shows that the models (in addition to the above) generally employed for the interpretation of phonon dispersion relations in sodium halides are RSM, DDM (deformation dipole model[35]), and BSGM (Basu and Sengupta[3] model) but none of them reproduces satisfactorily all the four frequency values at the zone-boundary points (X, L). If DDM and RSM calculations performed by Caldwell and Klein[34] for NaCl are compared with BSM, the latter gives a somewhat better fit. The RSM results, while reproducing the four frequency values at X, lead to very poor reproduction of LO and LA branches at the L point in NaCl crystal.

The degree of agreement achieved from ETSM in the present study is much better than that obtained by Singh and Verma[12] from the original TSM. This success is indicative of the fact that the extension and correction employed in TSM is important and essential for the adequate description of the dielectric and dynamical behavior of alkali halides.

The general conclusion drawn from the discussion of results on the prediction of phonon dispersion curves of sodium halides is that the ETSM incorporating the second-neighbor and three-body forces presents a useful description of the interatomic forces and gives a reasonable account of the deformation of outer electron shells in ionic crystals.

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