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Unified study of the lattice-mechanical properties of copper halide crystals

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The copper halide crystals, namely CuI, CuBr, and CuCl, though they have predominantly ionic binding, possess zinc-blende structure, and crystals having this structure have, in general, rather significantly low ionicity. This peculiarity is attendant with a number of unusual properties of this group of solids, and the various attempts to understand them in terms of the existing models show certain problems. Recently we have developed a general energy expression for an assembly of ions occupying an arbitrary configuration from a microscopic analysis of the problem. Inspection of the energy expression shows that within the S^2 approximation (up to and including second-order exchange) the following distortions are allowed: the two types of short-range dipolar deformations apart from the long-range dipolar one, scalar, and quadrupolar deformations. A model based on this energy expression has been employed to make a unified study of the different lattice-mechanical properties of the three copper halides. The specific properties that we have tried to correlate are the cohesive energy, the elastic and the dielectric properties, and the dispersion of phonons with the same set of parameters for each crystal. Finally, the results for the different crystals and the possible sources of the remaining discrepancies are discussed.

I. INTRODUCTION

The interpretation of the phonon dispersion relation of the copper halide crystals has recently been undertaken by several authors because of the peculiarities in their physical properties which are distinctly different from that of simple ionic crystals, as well as from crystals with the zinc-blende structure. Their ionic charge[1] is large, almost comparable to some alkali halides, being substantially higher than those of other materials with the zinc-blende- and wurtzite-type structures. The cuprous halides have low melting points comparable to those of Rb and Cs halides, while being comparatively low with respect to Ga compounds having the zinc-blende structure. In addition, the mixed conductivity, the superionic behavior,[2] the irregular value of thermal expansion coefficient with temperature,[3,4] a number of structural transitions with pressure[5] undergone in particular by the CuCl crystal and even the speculation of the CuCl crystal for being a candidate for a high-temperature superconductor,[6] have attracted considerable attention for an understanding of the physical processes in this group of solids. However, the entire emphasis in the study of the lattice dynamics of these crystals has been concentrated on the reproduction of the dispersion of phonons in terms of various types of polarizable models. In order to contribute to a better understanding of them, we should try to make a unified study of the static and dynamic properties in the framework of a single set of parameters. We have elsewhere discussed in a series of works[7-9] the importance of this type of study and the information it gives is more revealing than an attempt to reproduce very accurately only the phonon frequencies. So far no such attempt has been made in this direction for these solids. The major contention of the present study is to see how far it is possible to incorporate the different lattice mechanical properties of the three copper halide crystals, namely CuI, CuBr, and CuCl, within the framework of a single phenomenological model. We propose to make a microscopic analysis of the problem and attempt to construct a well-defined potential function for the energy of the crystal. Then this energy expression containing different terms, described in terms of parameters, may be put to a straight empirical test by calculating both the static and dynamic properties of the solid. Following the outline sketched above, we have successfully done such calculations for the AgCl (Ref. 10) and the NiO (Ref. 11) crystals, where the majority of terms have some *a priori* justification.

Prior to discussing our work, let us briefly appreciate the difficulties encountered in the investigations already carried out. Various versions of the rigid-ion model, shell model, and the deformation dipole model have been used to fit the lattice dynamics of these halides. The number of fitting parameters varies between six to fifteen. But all these models require a very low value of the ionic charge for the three Cu halides in order to obtain a fit to the phonon dispersion relation.

If the values of the ionic charge obtained by different authors[12–14] for the copper halides are used to estimate the cohesive energy it will lower the energy by an order of magnitude in the extreme case. Kunc *et al.*[15] and Hoshino *et al.*[13] have even obtained negative values of ionic charge (which is by definition positive). However, the cohesive energy is not a sensitive property for this group of solids and its agreement does not provide justification of the lattice dynamical models. In many models it is difficult to simultaneously reproduce the dispersion of phonons and the dielectric constants, e.g., in the work of Prevot *et al.*[12] the discrepancies in the elastic constants and the static and high-frequency dielectric constants are about 35–45 %. Vardeny *et al.*[16] obtained some improvement in the phonon description of CuCl by introducing an additional shell to treat the effect of the *d* electron in copper ions, but they have not taken into account any of the static properties. Jaswal[17] has obtained good agreement for dispersion curves of CuCl by introducing a screening factor to reduce the Coulomb interaction. But all the above models have been constructed after the force constant approach so that it is not possible to discuss the equilibrium condition of the lattice.

The broad common result emerging out of the above studies is that we require rather a high value of ionic charge to reproduce the cohesive energy of these solids and a quite low value of the ionic charge to have reasonable value of the phonon frequencies. The static charge, when the lattice is in equilibrium condition satisfying the symmetry of the crystal, is larger than the effective charge which comes into play when the symmetry is violated by lattice vibration. If we critically analyze the concept of charge deformation for an assembly of ions of arbitrary configuration, we may obtain the following elementary deformations: two types of short-range dipolar deformations, the long-range dipolar one, and the scalar and the quadrupolar deformations, all of which contribute to the properties of the lattice when the symmetry is violated by lattice vibration, but the dipolar and the quadrupolar deformations do not have any effect on the cohesion of a static lattice structure of a cubic crystal. Hence an analysis of the properties in the framework of a general potential function which incorporates the effects of these deformations may resolve the incompatibility just mentioned. It is important to mention here that a first-principles analysis[10,18] of the dipolar deformation of the charge cloud clearly shows that there are two different types of short-range dipole polarization effect and none of the works done so far has considered both of them. It is interesting to note that the short-range polarization effect which arises out of the overlap of the unperturbed wave functions corresponds to that of the deformation dipole model of Hardy and Karo[19] and the other short-range polarization effect due to the perturbed wave functions corresponds to that of the shell model.[20] The two dipoles having entirely different origin have separate effects on the properties and a complete theory must include both of them. Further, the effect of the quadrupolar deformation of ions has so far been neglected in the study of the lattice mechanics of the copper halides. The recent works by Kleppmann and Weber[21] and Ghosh *et al.*[10] on AgCl show the importance of this effect. It has also been demonstrated that the virtual *d-s* excitation of Ag^+ induced by the neighboring Cl^- leads to a quadrupolar deformability of its charge cloud. The Cu^+ has also a filled *d* shell and this deformability may be important for the study of copper halides. In fact, one of the major motivations of this work is to develop the relevant equations for incorporating the effect of quadrupolar polarizability for a zinc-blende structure crystal. In our previous works we have developed similar equations for the sodium chloride[22] and the cesium chloride[23] structure crystals and have found the effect to be important in several crystals.

In the next section we write down the general energy expression of an assembly of ions occupying arbitrary position, indicating briefly the origin of each term. Next we develop the energy expression corresponding to the quadrupolar and the scalar deformation of ions and calculate their contribution to the different static and dynamic properties. In the sections that follow, the complete model is applied to calculate the cohesive energy, the elastic constants, the dielectric constants, and the lattice dynamics of the three copper halides. In the last section we discuss the results of our calculation crystalwise, together with the success and limitations of the present approach for each of them.

II. MODEL

A. General energy expression

The basic approximation in writing the energy for an assembly of ions consists in assuming that the free ion wave functions may be regarded as a starting point and any change in the crystal environment may be treated as a perturbation. Then with the perturbed wave functions one may construct the Slater determinantal functions for the individual ions and then the Heitler-London-type antisymmetric wave functions for the whole crystal. Following the procedure outlined by Ghosh *et al.*[10] and Banerjee *et al.*,[18] the total Hamiltonian of the solid may be written as

$$H=H_0+V\,,$$

where (1)

$$V=\tfrac{1}{2}\sum_{G,G'}{}' V_{GG'}\,,$$

where H_0 is the Hamiltonian of the isolated ions and $V_{GG'}$ is the interaction between the nuclei and electrons of ions located at G and G' centers. It is to be noted that V does not represent the total potential energy of the ions. It represents only the interaction energy between the ions and is small compared to the energy of the isolated ions. The total energy for an assembly of such ions is given by

$$E=\frac{\int \tilde{\psi}_0 H \Phi_0 d\tau}{\int \tilde{\psi}_0 \Phi_0 d\tau}$$

where (2)

$$\Phi_0=\prod_G \Phi_G \quad \text{and} \quad \psi_0=A\Phi_0$$

in an obvious notation as defined in Ref. 10. To include the effect of perturbation we introduce the following wave functions,

$$\Phi_0'=\Phi_0+\sum_G C_G\Phi_{(G,\nu)}+\sum_{G,G'} C_{GG'}\Phi_{(G,\nu;G',\nu')}\,, \tag{3}$$

where (G,ν) and $(G,\nu;G',\nu')$ are the excited states of the crystal in which only a G ion and G and G' ions are excited. Using Eq. (3) and making a multipole expansion of V, we expand E in terms of V and S^2. If we retain terms up to purely second order in V and first in S^2, i.e., up to and including second-order exhange, the total energy of ions for arbitrary configuration may be written as

$$\begin{aligned}W={}&\tfrac{1}{2}\sum_{i,j}{}'\frac{Z_iZ_j}{r_{ij}}-\sum_i\vec{\mu}_i\cdot\vec{\mathrm{E}}_i^{m}-\tfrac{1}{2}\sum_i\vec{\mu}_i\cdot\vec{\mathrm{E}}_i^{\mu}+\sum_i\frac{(\vec{\mu}_i^{\,c})^2}{2\alpha_i}-\sum_i Q_i\,\mathrm{grad}E_i-\tfrac{1}{2}\sum_{i,j}{}'\left[\frac{c_{ij}}{r_{ij}^6}+\frac{d_{ij}}{r_{ij}^8}\right]\\&+\tfrac{1}{2}\sum_{\substack{i,j\\ j,\,\mathrm{NN\ of}\ i}}{}'\phi\left[\left|\vec{\mathrm{r}}_{ij}-\frac{\vec{\mu}_i^{\,c}}{y_i}+\frac{\vec{\mu}_j^{\,c}}{y_j}\right|\right]+\tfrac{1}{2}\sum_{\substack{i,j\\ j,\,\mathrm{NN\ of}\ i}}{}'\phi(\vec{\mathrm{r}}_{ij})+\tfrac{1}{2}\sum_{\substack{i,j\\ j,\mathrm{NNN\ of}\ i}}\phi(\vec{\mathrm{R}}_{ij})\\&+\tfrac{1}{2}\sum_{j,m}{}'\sum_{\substack{i\\ (\mathrm{NN\ both\ of}\ j\ \mathrm{and}\ m)}}A(k)\exp\left[-\frac{(r_{ij}+r_{im})}{\rho}\right]\,,\end{aligned} \tag{4}$$

where $\vec{\mu}_i=\vec{\mu}_i^{\,d}+\vec{\mu}_i^{\,c}$ represents the total dipole moment of the ith ion; $\vec{\mu}_i^{\,d}$ is the deformation dipole arising out of the first-order exchange interaction due to overlap of the ground-state wave functions of the ions and $\vec{\mu}_i^{\,c}$ is the dipole moment due to the perturbed wave functions. $\vec{\mathrm{E}}_i^{m}$ and $\vec{\mathrm{E}}_i^{\mu}$ represent the monopole and dipole fields due to all other ions at the lattice site i. α_i is the polarizability of the ith ion, c_{ij} and d_{ij} represent the dipole and the quadrupole van der Waals coefficients for the i-j ion pair. Here $\vec{\mathrm{r}}_{ij}=\vec{\mathrm{r}}_i-\vec{\mathrm{r}}_j$ is the distance between the ith and jth ions. Z_i is the static ionic charge of the ith ion. The first three terms represent the pure electrical interactions and the fourth term represents the self-energy corresponding to the electric dipole. The fifth term is the interaction of the quadrupole moment Q_i with the electric field E_i due to monopoles and dipoles of other ions. The sixth term represents the van der Waals interaction. The seventh term is the changes in the nearest-neighbor overlap interaction due to formation of dipole moments by the perturbation of their wave functions. The eighth and the ninth terms represent the usual overlap interaction between the nearest-neighbor and the second-neighbor ions, respectively. The last term represents an effective three-body interaction between the ions, arising out of the scalar deformation of the charge cloud. $A(k)$ is some constant which measures the deformability of the kth-type ion. We have neglected the modifications of the van der Waals interaction, the second-neighbor overlap interaction, and the three-body interaction due to the presence of dipoles $\vec{\mu}_i^{\,c}$ in the ions. The modification has been retained only in the dominant term of the energy, namely, the nearest-neighbor overlap interaction. The detailed calculation of the derivation of Eq. (4) from Eq. (2) has been discussed in Refs. 10 and 18. We shall now employ our energy expression (4) to study the different properties of the copper halides. In the next section we develop the relevant equations to incorporate the effect of the quadrupolar and scalar deformations.

B. Energy expression due to quadrupolar deformation

The theory of the effect of quadrupolar deformation of the charge cloud in centrosymmetric crystals has been developed by Ghosh *et al.*[23] In the following we develop the same in case of noncentrosymmetric structure crystals (zinc blende). The change in total energy of an assembly of ions due to quadrupolar deformation of the charge cloud consists of changes in (a) the multipole electrostatic energy, (b) the self-energy, and (c) the short-range overlap energy in decreasing order of magnitude. We shall consider only the first effect. Now the quadrupolar moment in an ion may be generated due to (a) an overlap between the unperturbed wave functions of the nearest neighbors; this is the exchange quadrupole, and (b) perturbation of the wave function by the gradient of the electric field produced by the other ions; this is the electrical quadrupole. It is difficult to judge *a priori* the relative importance of these two effects. However, our preliminary investigation for the CsI crystal indicates that the second effect is negligible. However, since we shall treat this effect by parametrization we need not go into its detailed mechanism.

The exchange quadrupole originates by making a multipole expansion of the exchange charge distribution and we locate it on the ion centers similar to that of the exchange dipole. Consequently, there will be no self-energy associated with this quadrupolar deformation. Now following the treatment of Ghosh *et al.*[23] we write the short-range quadrupolar moment $q^s_{\alpha\beta}(l,k)$ in an ion (l,k) due to the displacement of its nearest neighbors,

$$q^s_{\alpha\beta}(l,k)=\sum_{l',k'}{}' d_k \Phi^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} u_\gamma \begin{bmatrix} l & l' \\ k & k' \end{bmatrix}, \tag{5}$$

where $u\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)$ is the displacement of the $(l'k')$ ion relative to ion l,k, d_k is the parameter denoting the quadrupolar polarizability of the kth-type ion, and the third rank tensor $\Phi^s_{\alpha\beta\gamma}\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)$ is related to the nearest-neighbor overlap interaction by

$$\Phi^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}=\frac{\partial}{\partial r_\alpha \begin{bmatrix} l \\ k \end{bmatrix}}\frac{\partial}{\partial r_\beta \begin{bmatrix} l \\ k \end{bmatrix}}\left[\phi\left[r\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\right]\right] \times r_\gamma \begin{bmatrix} l & l' \\ k & k' \end{bmatrix} \tag{6}$$

where $\phi\left(r\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)\right)$ represents the nearest-neighbor overlap given by the Born-Mayer potential $b\exp(-r/\rho)$ and $r\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)$ the separation between ions l,k and l',k'. b and ρ are the short-range repulsive interaction parameters. We rewrite Eq. (5) as

$$q^s_{\alpha\beta}(l,k)=\sum_{l'k'\gamma} d_k \lambda^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} u_\gamma \begin{bmatrix} l' \\ k' \end{bmatrix}, \tag{7a}$$

where

$$\lambda^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}=-\Phi^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}(1-\delta_{ll'}\delta_{kk'}) + q'^s_{\alpha\beta\gamma}\delta_{ll'}\delta_{kk'} \tag{7b}$$

and

$$q'^s_{\alpha\beta\gamma}=\sum_{l'k'}{}'\Phi^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}.$$

Here α,β,γ denote Cartesian components.

The last term in Eq. (7b) exists in noncentrosymmetric structures only when $\alpha\neq\beta\neq\gamma$. Since there is no self-energy associated with the exchange quadrupole, the energy of interaction is given by

$$W^{q^s}=-\sum_{l,k} q^s \begin{bmatrix} l \\ k \end{bmatrix} \operatorname{grad} E \begin{bmatrix} l \\ k \end{bmatrix}, \tag{8}$$

where the total field gradient at the site (l,k) due to monopole and dipole charges is given by (quadrupole-quadrupole effect is neglected)

$$E_{\alpha\beta}\begin{bmatrix} l \\ k \end{bmatrix}=\sum_{l',k',\gamma}\Phi^m_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} u_\gamma \begin{bmatrix} l' \\ k' \end{bmatrix} - \sum_{l',k',\gamma}\Phi_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} \mu_\gamma \begin{bmatrix} l' \\ k' \end{bmatrix} \tag{9}$$

and the first and the second terms on the right-hand side of Eq. (9) represent the field gradients due to monopole and dipole charges, respectively. These are written as

$$\Phi^m_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}=\left[-\Phi_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}(1-\delta_{ll'}\delta_{kk'}) + \psi_{\alpha\beta\gamma}\delta_{ll'}\delta_{kk'}\right] Z_{k'}, \tag{10}$$

where

$$\psi_{\alpha\beta\gamma}=\sum_{l'k'}{}'\Phi_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}$$

and $Z_{k'}$ is the ionic charge of k'-type ion. The above term exists for the noncentrosymmetric structure only when $\alpha\neq\beta\neq\gamma$.

The term $\Phi_{\alpha\beta\gamma}\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)$ is given by

$$\Phi_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} = \frac{\partial}{\partial r_\alpha\begin{bmatrix} l \\ k \end{bmatrix}}\frac{\partial}{\partial r_\beta\begin{bmatrix} l \\ k \end{bmatrix}}\frac{\partial}{\partial r_\gamma\begin{bmatrix} l' \\ k' \end{bmatrix}}\left[-\frac{1}{r\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}}\right]\Bigg|_{r\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)=r_0\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)}$$

$$= 15 r_{0\alpha}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} r_{0\beta}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} r_{0\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} \Big/ r_0^7\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}$$

$$-3\left[r_{0\alpha}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\delta_{\beta\gamma} + r_{0\beta}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\delta_{\alpha\gamma} + r_{0\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\delta_{\alpha\beta}\right]\Big/ r_0^5\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}, \qquad (11)$$

where $r_0\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)$ is the equilibrium value of $r\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right)$. So, using the above equations we may write the additional energy due to quadrupolar interaction as

$$W^{q^s} = \sum_{\substack{l'k',l''k'' \\ \gamma\delta}}\left[\frac{1}{2}\Phi^{s(1)}_{\gamma\delta}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix} u_\gamma\begin{bmatrix} l' \\ k' \end{bmatrix} u_\delta\begin{bmatrix} l'' \\ k'' \end{bmatrix} + \Phi^{s(2)}_{\gamma\delta}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix} u_\gamma\begin{bmatrix} l' \\ k' \end{bmatrix} u_\delta\begin{bmatrix} l'' \\ k'' \end{bmatrix}\right], \qquad (12)$$

where

$$\Phi^{s(1)}_{\gamma\delta}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix} = -\sum_{\substack{l,k \\ \alpha,\beta}}\left[d_k\lambda^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\Phi^m_{\alpha\beta\delta}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix} + d_k\lambda^s_{\alpha\beta\delta}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix} \times \Phi^m_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\right] \qquad (13)$$

and

$$\Phi^{s(2)}_{\gamma\delta}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix} = \sum_{\substack{l,k, \\ \alpha,\beta}}{}' d_k\lambda^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\Phi_{\alpha\beta\delta}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix}, \qquad (14)$$

where

$$\sum{}' \Longrightarrow l,k \neq l'',k'' .$$

It is evident from Eq. (12) that this energy vanishes when the lattice is in equilibrium configuration and hence this interaction does not contribute anything to the cohesion of the lattice. But it will contribute to the vibrational and other properties of the lattice. In the following sections we work out the relevant equations for them.

C. Contribution to elastic constants from quadrupolar deformation

The contribution to the elastic constants due to quadrupolar deformation is obtained by the method[24] of long waves due to Born. Since dipole polarization has no effect on the cohesive energy and elastic constants of a static lattice of a cubic crystal, in order to obtain the quadrupolar contribution to the elastic constants we assume a rigid-ion model. Putting $\mu=0$ in the force constants defined above, we evaluate the following terms in brackets (for notation and details see Born and Huang[24]),

$$[\delta\gamma\mu\nu] = -\frac{1}{2v_0}\sum_{\substack{k' \\ l'',k''}}\Phi^{s(1)}_{\gamma\delta}\begin{bmatrix} l'' & l' \\ k'' & k' \end{bmatrix} r_\mu\begin{bmatrix} l'' & l' \\ k'' & k' \end{bmatrix} \times r_\nu\begin{bmatrix} l'' & l' \\ k'' & k' \end{bmatrix}, \qquad (15)$$

where v_0 is the volume per unit cell and $r\left(\begin{smallmatrix} l & l' \\ k & k' \end{smallmatrix}\right) = r\left(\begin{smallmatrix} l \\ k \end{smallmatrix}\right) - r\left(\begin{smallmatrix} l' \\ k' \end{smallmatrix}\right)$. Substituting the force constants from (13) in Eq. (15) we get

$$[\delta\gamma\mu\nu] = \frac{1}{2v_0}\sum_{\substack{k';l'',k''; \\ l,k;\alpha,\beta}}\left[d_k\lambda^s_{\alpha\beta\delta}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix}\Phi^m_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} + d_k\lambda^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\Phi^m_{\alpha\beta\delta}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix}\right]$$

$$\times\left[r_\mu\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} - r_\mu\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix}\right]\left[r_\nu\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} - r_\nu\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix}\right]. \qquad (16)$$

To simplify these expressions we use more compact notations by introducing the following terms in curly brackets:

$$\begin{aligned}
\{\alpha\beta\gamma\} &= \sum_{l',k'} \Phi^{m}_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} , \\
\{\alpha\beta\gamma\mu\} &= \sum_{l',k'} \Phi^{m}_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} r_\mu \begin{bmatrix} l & l' \\ k & k' \end{bmatrix} , \\
\{\alpha\beta\gamma\mu\nu\} &= \sum_{l',k'} \Phi^{m}_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} r_\mu \begin{bmatrix} l & l' \\ k & k' \end{bmatrix} r_\nu \begin{bmatrix} l & l' \\ k & k' \end{bmatrix} ,
\end{aligned} \tag{17}$$

and

$$\{\alpha\beta\gamma\}^{s} = \sum_{l',k'} \lambda^{s}_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix} .$$

and so on for the terms in brackets with superscript S. In terms of the curly brackets expression (16) reduces to

$$\begin{aligned}
[\delta\gamma\mu\nu] = \frac{1}{2v_0}\sum_{k,\alpha,\beta} d_k (&\{\alpha\beta\delta\}^{s}\{\alpha\beta\gamma\mu\nu\} - \{\alpha\beta\delta\nu\}^{s}\{\alpha\beta\gamma\mu\} - \{\alpha\beta\delta\mu\}^{s}\{\alpha\beta\gamma\nu\} \\
&+ \{\alpha\beta\delta\mu\nu\}^{s}\{\alpha\beta\gamma\} + \{\alpha\beta\gamma\mu\nu\}^{s}\{\alpha\beta\delta\} - \{\alpha\beta\gamma\mu\}^{s}\{\alpha\beta\delta\nu\} \\
&- \{\alpha\beta\gamma\nu\}^{s}\{\alpha\beta\delta\mu\} + \{\alpha\beta\gamma\}^{s}\{\alpha\beta\delta\mu\nu\}) .
\end{aligned} \tag{18}$$

Since both the short-range and the long-range sums denoted by $\{\alpha\beta\gamma\}$ and $\{\alpha\beta\gamma\mu\nu\}$ vanish for the zinc-blende structure, we finally get the general expression for the elastic constants as

$$\begin{aligned}
[\delta\gamma\mu\nu] = -\frac{1}{2v_0}\sum_{k,\alpha,\beta} d_k (&\{\alpha\beta\delta\nu\}^{s}\{\alpha\beta\gamma\mu\} \\
&+ \{\alpha\beta\delta\mu\}^{s}\{\alpha\beta\gamma\nu\} \\
&+ \{\alpha\beta\gamma\mu\}^{s}\{\alpha\beta\delta\nu\} \\
&+ \{\alpha\beta\gamma\nu\}^{s}\{\alpha\beta\delta\mu\}) .
\end{aligned} \tag{19}$$

Using Eq. (19) the contribution of quadrupolar deformation to the individual elastic constants is given by (neglecting the contribution of quadrupolar deformation to internal strain)

$$\begin{aligned}
C_{11} &= [1111] \\
&= -\frac{2}{v_0}(d_+ - d_-)(\{1111\}\{1111\}^{s} \\
&\qquad + 2\{2211\}\{2211\}^{s})
\end{aligned}$$

and (20)

$$\begin{aligned}
C_{44} &= [1122] \\
&= -\frac{2}{v_0}(d_+ - d_-)(\{1212\}\{1212\}^{s} \\
&\qquad + \{2112\}\{2112\}^{s})
\end{aligned}$$

where d_+ and d_- are the quadrupolar polarizability parameters of positive and negative ions, respectively, and C_{12} is calculated from the bulk modulus using the relation

$$B = C_{11} + 2C_{12} = 0 .$$

The method of evaluation of the long-range lattice sums is discussed in Appendix A and the relevant sums are given in Table I.

D. Contribution to lattice dynamics from quadrupolar deformation

In this section we calculate the contribution to the dynamical matrix from the quadrupolar deformation energy. The dynamical matrices $Q^{(1)}_{\gamma\delta}(k'k'')$ and $Q^{(2)}_{\gamma\delta}(k'k'')$ corresponding to the force constants $\Phi^{s(1)}_{\gamma\delta}\binom{l' \ \ l''}{k' \ \ k''}$ and $\Phi^{s(2)}_{\gamma\delta}\binom{l' \, l''}{k' k''}$ defined earlier, may be

TABLE I. Lattice sums for calculating elastic constants.

$\sum_l{}' \frac{1}{l^3} e^{-i(l,\pi)}$	$\sum_l{}' \frac{l_1^4}{l^7} e^{-i(l,\pi)}$	$\sum_l{}' \frac{l_1^2 l_2^2}{l^7} e^{-i(l,\pi)}$
-4.16764	-0.42028	-0.48837

written as

$$Q^{(1)}_{\gamma\delta}(k'k'')=\sum_{l''}\Phi^{s(1)}_{\gamma\delta}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix} \times\exp\left[-i\vec{q}\cdot\vec{r}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix}\right] \tag{21}$$

and

$$Q^{(2)}_{\gamma\delta}(k'k'')=\sum_{l''}\Phi^{s(2)}_{\gamma\delta}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix} \times\exp\left[-i\vec{q}\cdot\vec{r}\begin{bmatrix} l' & l'' \\ k' & k'' \end{bmatrix}\right] . \tag{22}$$

After some straightforward manipulation Eqs. (21) and (22) are given by

$$\begin{aligned} Q^{(1)}_{\gamma\delta}(k'k'')=\sum_{\alpha,\beta}\Bigg[&-\sum_k d_k Q^s_{\alpha\beta\gamma}(kk')Q_{\alpha\beta\delta}(kk'')Z_{k''} \\ &+Z_{k''}[d_{k''}Q^s_{\alpha\beta\gamma}(k''k')\psi_{\alpha\beta\delta}+d_{k'}q'^s_{\alpha\beta\gamma}Q_{\alpha\beta\delta}(k'k'')](1-\delta_{l'l''}\delta_{k'k''}) \\ &-d_{k'}Z_{k''}q'^s_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}\delta_{k'k''}\delta_{l'l''}+(\gamma\leftrightarrow\delta,k'\leftrightarrow k'')\Bigg] \\ &+\sum_{\alpha,\beta}(d_{k'}+d_k)(q'^s_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}Z_{k''}+q'^s_{\alpha\beta\delta}\psi_{\alpha\beta\gamma}Z_{k'}) \end{aligned} \tag{23}$$

and

$$\begin{aligned} Q^{(2)}_{\gamma\delta}(k'k'')=&\sum_{k,\alpha,\beta}-d_k Q^s_{\alpha\beta\gamma}(kk')Q_{\alpha\beta\delta}(kk'')+\sum_{\alpha,\beta}d_{k'}q'^s_{\alpha\beta\gamma}Q_{\alpha\beta\delta}(k'k'') \\ &+\sum_{\alpha,\beta}d_{k''}q'^s_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}(1-2\delta_{k'k''}) , \end{aligned} \tag{24}$$

where

$$Q^s_{\alpha\beta\gamma}(kk')=\sum_l{}'\Phi^s_{\alpha\beta\gamma}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\exp\left[i\vec{q}\cdot\vec{r}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}\right]$$

and (25)

$$Q_{\alpha\beta\delta}(kk'')=\sum_{l''}{}'\Phi_{\alpha\beta\delta}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix}\exp\left[-i\vec{q}\cdot\vec{r}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix}\right] .$$

The individual elements are given by

$$\begin{aligned} Q^{(1)}_{\gamma\delta}(11)=&-\sum_{\alpha,\beta}[d_-Q^s_{\alpha\beta\gamma}(21)Q_{\alpha\beta\delta}(21)+d_+q'^s_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}+d_-Q^s_{\alpha\beta\delta}(12)Q_{\alpha\beta\gamma}(12)+d_+q'^s_{\alpha\beta\delta}\psi_{\alpha\beta\gamma}]Z_1 \\ &+\sum_{\alpha,\beta}(d_++d_-)Z_1(q'^s_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}+q'^s_{\alpha\beta\delta}\psi_{\alpha\beta\gamma}) , \end{aligned} \tag{26a}$$

$$\begin{aligned} Q^{(1)}_{\gamma\delta}(22)=&-\sum_{\alpha,\beta}[d_+Q^s_{\alpha\beta\gamma}(12)Q_{\alpha\beta\delta}(12)+d_+Q^s_{\alpha\beta\delta}(21)Q_{\alpha\beta\gamma}(21)+d_-q'^s_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}+d_-q'^s_{\alpha\beta\delta}\psi_{\alpha\beta\gamma}]Z_2 \\ &+\sum_{\alpha,\beta}(d_++d_-)Z_2(q'^s_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}+q'^s_{\alpha\beta\delta}\psi_{\alpha\beta\gamma}) , \end{aligned} \tag{26b}$$

$$Q^{(1)}_{\gamma\delta}(12)=\sum_{\alpha,\beta}\{[d_-Q^{s}_{\alpha\beta\gamma}(21)\psi_{\alpha\beta\delta}+d_+q'^{s}_{\alpha\beta\gamma}Q_{\alpha\beta\delta}(12)]Z_2$$
$$+[d_+Q^{s}_{\alpha\beta\delta}(12)\psi_{\alpha\beta\gamma}+d_-q'^{s}_{\alpha\beta\delta}Q^{s}_{\alpha\beta\gamma}(21)]Z_1$$
$$+(d_+ +d_-)(q'^{s}_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}Z_2+q'^{s}_{\alpha\beta\delta}\psi_{\alpha\beta\gamma}Z_1)\}\ , \tag{26c}$$

$$Q^{(2)}_{\gamma\delta}(11)=-\sum_{\alpha,\beta}[d_-Q^{s}_{\alpha\beta\gamma}(21)Q_{\alpha\beta\delta}(21)-d_+q'^{s}_{\alpha\beta\gamma}Q_{\alpha\beta\delta}(11)]-\sum_{\alpha,\beta}d_+q'^{s}_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}\ , \tag{27a}$$

$$Q^{(2)}_{\gamma\delta}(22)=-\sum_{\alpha,\beta}[d_+Q^{s}_{\alpha\beta\gamma}(12)Q_{\alpha\beta\delta}(12)-d_-q'^{s}_{\alpha\beta\gamma}Q_{\alpha\beta\delta}(22)]-\sum_{\alpha,\beta}d_-q'^{s}_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}\ , \tag{27b}$$

$$Q^{(2)}_{\gamma\delta}(21)=-\sum_{\alpha,\beta}[d_+Q^{s}_{\alpha\beta\gamma}(12)Q_{\alpha\beta\delta}(11)-d_-q'^{s}_{\alpha\beta\gamma}Q_{\alpha\beta\delta}(21)]+\sum_{\alpha,\beta}d_+q'^{s}_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}\ , \tag{27c}$$

and

$$Q^{(2)}_{\gamma\delta}(12)=-\sum_{\alpha,\beta}[d_-Q^{s}_{\alpha\beta\gamma}(21)Q_{\alpha\beta\delta}(22)-d_+q'^{s}_{\alpha\beta\gamma}Q_{\alpha\beta\delta}(12)]+\sum_{\alpha,\beta}d_-q'^{s}_{\alpha\beta\gamma}\psi_{\alpha\beta\delta}\ . \tag{27d}$$

Indices 1 and 2 refer to the two particles on the two different sublattices. The method of evaluation of the periodic long-range sums in the above equations is discussed in Appendix A and the relevant sums which are of general interest are given in Table II.

Unlike the other cubic crystals with a center of symmetry the effect of quadrupolar deformation does not vanish in the limit of long-wavelength optical vibrations. Hence quadrupolar deformation contributes also to the dielectric properties of these crystals which we shall discuss in a later section.

E. Scalar deformation and its contribution to different properties

The last term of our general energy expression (4) represents an effective three-body interaction between the ions generated out of the isotropic deformation of the charge cloud. Ghosh and Basu[7] have derived the form given in (4) from a statistical model analysis of the charge distribution inside a crystal. It is shown in Refs. 25 and 26 that the dominant contribution of the breathing degree of freedom of the electron charge cloud in the breathing shell model[27] generates an effective three-body interaction which is identical to the above form. The effect of this deformation has been found to be quite important in various types of crystals.[7–10] But so far there has been no attempt to investigate its effect on the properties of ionic crystals with zinc-blende structure. Unlike the quadrupolar deformation it will contribute to the cohesive energy. Starting from the expression given in Eq. (4) it is quite straightforward to obtain its contribution to the elastic constants which is given later in the final expression for the elastic constants. In this section we calculate its contribution to the dynamical matrix. Denoting the last term of Eq. (4), the energy due to scalar deformation by E^s, the general expression for the force constant is given by

$$\Phi^{s}_{\alpha\beta}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix}=\frac{\partial^2 E^s}{\partial r_\alpha \begin{bmatrix} l \\ k \end{bmatrix} \partial r_\beta \begin{bmatrix} l' \\ k' \end{bmatrix}}=-\sum_{\substack{l'',k'' \\ \text{NN of } l,k}}[(r_1)_\alpha(r_1)_\beta D_1^2+\delta_{\alpha\beta}D_1+(r_1)_\beta(r_2)_\alpha D_1D_2]\phi(r_1,r_2)$$
$$-\sum_{\substack{l'',k'' \\ \text{NN of } l'k'}}[(r_1)_\alpha(r_1)_\beta D_1^2+\delta_{\alpha\beta}D_1+(r_3)_\beta(r_1)_\alpha D_1D_3]\phi(r_1,r_3)\ , \tag{28}$$

where

$$\vec{r}_1=\vec{r}\begin{bmatrix} l & l' \\ k & k' \end{bmatrix},\quad \vec{r}_2=\vec{r}\begin{bmatrix} l & l'' \\ k & k'' \end{bmatrix},\quad \vec{r}_3=\vec{r}\begin{bmatrix} l'' & l' \\ k'' & k' \end{bmatrix},\quad D=\frac{1}{r}\frac{d}{dr}$$

and

$$\phi(r_1,r_2)=A(k)\exp[-(r_1+r_2)/\rho]\ .$$

TABLE II. (a) Lattice sums for ZnS structure. (b) Lattice sums for ZnS structure: ⟨111⟩ direction. $l_1 l_2 l_3$ denote coordinates of the lattice points of a ZnS lattice. In ⟨100⟩ direction, interchange between l_2 and l_3, in ⟨111⟩ direction interchange between l_1, l_2, and l_3, and in ⟨110⟩ direction, interchange between l_1 and l_2 leaves the sums unaffected.

(a)

α	$\sum_l' \frac{l_1^3}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1}{l^5} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1 l_2^2}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1 l_2 l_3}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1 l_3^2}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1^2 l_3}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_3^3}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_3}{l^5} \times e^{-i(l,\alpha)}$
1000	$-0.9835i$	$-3.8656i$	$-1.4604i$	0.0	$-1.4604i$	0.0	0.0	0.0
800	$-1.0362i$	$-3.8238i$	$-1.3941i$	0.4196	$-1.3941i$	0.0	0.0	0.0
600	$-1.1596i$	$-3.7182i$	$-1.2807i$	0.7849	$-1.2807i$	0.0	0.0	0.0
400	$-1.2521i$	$-3.3942i$	$-1.0697i$	1.0587	$-1.0697i$	0.0	0.0	0.0
200	$-1.1184i$	$-2.5592i$	$-0.7172i$	1.2254	$-0.7172i$	0.0	0.0	0.0
000	0.0	0.0	0.0	1.2810	0.0	0.0	0.0	0.0
660	$-0.6823i$	$-1.9248i$	$-0.5416i$	0.4915	$-0.7001i$	−0.8439	−0.6922	−2.3809
440	$-0.9565i$	$-2.3528i$	$-0.6104i$	0.8801	$-0.7866i$	−0.4141	−0.3795	−1.2062
220	$-0.9763i$	$-2.0875i$	$-0.4944i$	1.1724	$-0.6129i$	−0.1093	−0.1070	−0.3242

(b)

α	$\sum_l' \frac{l_1^3}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1}{l^5} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1 l_2^2}{l^7} \times e^{-i(l,\alpha)}$	$\sum_l' \frac{l_1 l_2 l_3}{l^7} \times e^{-i(l,\alpha)}$
555	$-0.569(1+i)$	$-1.4333(1+i)$	$-0.4351(1+i)$	$0.5432(1+i)$
444	$-0.3904-0.7284i$	$-1.0501-1.7411i$	$-0.3302-0.5071i$	$0.7476+0.3600i$
333	$-0.2324-0.8434i$	$-0.6508-1.7004i$	$-0.2113-0.5240i$	$0.9510+0.2156i$
222	$-0.1077-0.8604i$	$-0.3125-1.4756i$	$-0.1032-0.4721i$	$1.1236+0.1135i$
111	$-0.0276-0.6965i$	$-0.0831-0.9444i$	$-0.0273-0.3321i$	$1.2470+0.0610i$

For the ZnS structure, the nonvanishing value of the scalar deformation force constants between l',k' and l'',k'' exist only when $k''=k'$ and $l''=l'$ or l'',k'' is an ion of type a as shown in Fig. 1. The corresponding force constant matrix is given by

$$\Phi^s\begin{bmatrix} l' & \\ & a \\ k' & \end{bmatrix}=\frac{A(k)}{3\rho^2}\exp\left[-\frac{2r}{\rho}\right]\begin{bmatrix} -1 & -1 & 1 \\ -1 & -1 & 1 \\ -1 & -1 & 1 \end{bmatrix} \tag{29}$$

and the force constant matrix between the nearest neighbors because of this interaction is given by

$$\Phi^s\begin{bmatrix} l' & l \\ k' & k \end{bmatrix}=-[A(k)+A(k')]\exp\left[-\frac{2r}{\rho}\right]\begin{bmatrix} \frac{2}{3\rho^2}-\frac{2}{\rho r} & \frac{2}{3\rho^2}+\frac{1}{\rho r} & \frac{2}{3\rho^2}+\frac{1}{\rho r} \\ \frac{2}{3\rho^2}+\frac{1}{\rho r} & \frac{2}{3\rho^2}-\frac{2}{\rho r} & \frac{2}{3\rho^2}+\frac{1}{\rho r} \\ \frac{2}{3\rho^2}+\frac{1}{\rho r} & \frac{2}{3\rho^2}+\frac{1}{\rho r} & \frac{2}{3\rho^2}-\frac{2}{\rho r} \end{bmatrix}, \tag{30}$$

where $A(k)$ and $A(k')$ are parameters describing the scalar deformation of the charge cloud of the two types of ions. The contribution to dynamical matrix because of the force constants (29) is given by

$$\begin{aligned} M^s_{\alpha\alpha}(k'',k')&=4P(k)\delta(k'',k')[\cos(q_\beta a)\cos(q_\gamma a)-\cos(q_\alpha a)\cos(q_\beta a)-\cos(q_\alpha a)\cos(q_\gamma a)+1]\,,\\ M^s_{\alpha\beta}(k'',k')&=4P(k)\delta(k'',k')\{\sin(q_\alpha a)\sin(q_\beta a)+i\sin(q_\gamma a)[\cos(q_\alpha a)-\cos(q_\beta a)]\}\,, \end{aligned} \tag{31}$$

where $2a$ is the lattice constant, $k=k'$, and k,k',k'' take up values 1 and 2 corresponding to positive or negative ions and

$$P(k)=\frac{A(k)}{3\rho^2}\exp\left[-\frac{2r}{\rho}\right]. \tag{32}$$

The additional two-body interaction given by (30) is treated in a similar way as that of the nearest-neighbor repulsive interaction.

Unlike the quadrupolar deformation, discussed in the preceding section, the scalar deformation effects vanish in the limit of long-wavelength optical vibration and consequently do not contribute anything to the dielectric properties of the zinc sulfide structure crystals.

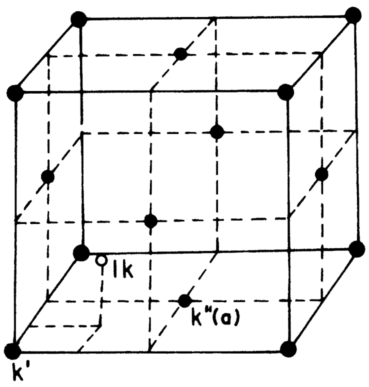

FIG. 1. Position of particle (a) for which nonvanishing force constants exist in a ZnS structure. Other particles are obtained from symmetry.

Now we are able to discuss both the lattice statics and the dynamics of copper halides with the help of the energy expression (4) together with the equations in Secs. II D and II E provided we use the adiabatic condition,

$$\partial W/\partial \mu_i=0\,. \tag{33}$$

In the final application we have made some simplifying assumptions in order to keep the number of parameters as small as possible and also to ensure that the essential physical picture is not lost in mathematical complexity. Since in all the three halides the dipolar polarizability of the copper ion is much smaller than that of the halides, we consider only the negative ion polarizable. Both the dipole polarizabilities due to exchange charge and perturbation of the wave function are associated with the anion. The three-body interaction generated out of the scalar deformation has been confined to the case only when the interacting ions have common nearest neighbor. The second-neighbor overlap has been assumed to act between the anions only. Fixing the value of the static ionic charge to unity, the present model contains eleven adjustable parameters: b and ρ, the short-range overlap parameters: c and ρ', the parameters describing the deformation dipole arising from the exchange charge; α and y, the parameters for the dipole due to perturbation of wave functions; d_+ and d_-, the parameters for the quadrupolar polarizabilities of the two types of ions; $A(1)$ and $A(2)$, the scalar deformation parameters; and b' and ρ, the overlap interaction parameters between anions. The values of the parameters are given in Table III. In the present investigation we are not looking for an exact fit of some properties, rather we want to see how far it is possible to reproduce a gross overall description of different properties in terms of a single set of parameters. So the approximations mentioned above will not seriously affect our conclusion.

III. COHESION AND ELASTIC PROPERTIES

From the general expression for energy (4) for an assembly of ions occupying arbitrary configuration, we can write down the energy per unit cell for a zinc-blende structure lattice in equilibrium configuration. From the symmetry of the lattice the dipole and quadrupole terms vanish and the static lattice energy per unit cell is given by

$$\Phi_{\mathrm{ZnS}}=-\alpha_{\mathrm{ZnS}}\frac{e^2}{\tilde{r}}+4b\exp\left[-\frac{\tilde{r}}{\rho}\right]+12b'\exp\left[-\frac{\tilde{R}}{\rho}\right]+4c_{+-}/\tilde{r}^6-4d_{+-}/\tilde{r}^8+6A\exp(-2\tilde{r}/\rho)\;, \tag{34}$$

TABLE III. Values of the parameters.

Parameters	CuI	CuBr	CuCl
b (10^{-8} erg)	6.58	0.7119	0.303
b' (10^{-7} erg)	56.94	0.7942	0.1054
ρ (10^{-8} cm)	0.2150	0.2533	0.273
y (D)	6.4098	2.7237	2.8973
α (10^{-24} cm^3)	8.7587	7.4008	5.1954
c (10^{-8} D)	0.7386	0.3064	0.0876
ρ_1 (10^{-8} cm)	2.4	2.4	2.5
$A(1)$ (10^{-6} erg)	273.4	3.228	1.5828
$A(2)$ (10^{-6} erg)	-273.4	0.0	-1.5828
d_+ (10^{-23} dyn cm^4)	-4.0	-0.4	-0.2
d_- (10^{-23} dyn cm^4)	4.026	0.0	0.1

where e is the electronic charge, $A=A(1)+A(2)$, c_{+-} and d_{+-} are the van der Waals coefficients, and $\tilde{r}$ and $\tilde{R}$ are the harmonic nearest-neighbor and second-nearest-neighbor distances, respectively. We have used the harmonic values since we neglect the vibration part of the energy.[28] The expression for the second-order elastic constants is calculated from the general energy expression together with Eq. (20) and is given below

$$C_{11}=\frac{\sqrt{3}}{4\tilde{r}}\left\{\frac{1}{3}\left[\frac{b}{\rho}\exp\left[-\frac{\tilde{r}}{\rho}\right]\left[\frac{1}{\rho}-\frac{2}{\tilde{r}}\right]-\frac{30c_{+-}}{\tilde{r}^8}-\frac{56d_{+-}}{\tilde{r}^{10}}\right.\right.$$
$$\left.\left.+\frac{4b'}{\rho}\exp\left[-\frac{\tilde{R}}{\rho}\right]\left[\frac{1}{\rho}-\frac{1}{\tilde{R}}\right]+\frac{2}{\rho}A(r)\left[\frac{1}{\rho}-\frac{1}{\tilde{r}}\right]\right]\right\}+0.035\frac{e^2Z^2}{\tilde{r}^4}\;, \tag{35a}$$

$$C_{12}=\frac{\sqrt{3}}{4\tilde{r}}\left\{\frac{1}{3}\left[\frac{b}{\rho}\exp\left[-\frac{\tilde{r}}{\rho}\right]\left[\frac{1}{\rho}+\frac{4}{\tilde{r}}\right]-\frac{66c_{+-}}{\tilde{r}^8}-\frac{104d_{+-}}{\tilde{r}^{10}}\right.\right.$$
$$\left.\left.+\frac{2b'}{\rho}\exp\left[-\frac{\tilde{R}}{\rho}\right]\left[\frac{1}{\rho}+\frac{5}{\tilde{R}}\right]+\frac{2}{\rho}\left[\frac{1}{\rho}+\frac{2}{\tilde{r}}\right]A(r)\right]\right\}-0.3726\frac{e^2Z^2}{\tilde{r}^4}\;, \tag{35b}$$

$$C_{44}=\frac{\sqrt{3}}{4\tilde{r}}\left[\frac{1}{3}\left[\frac{b}{\rho}\exp\left[-\frac{\tilde{r}}{\rho}\right]\left[\frac{1}{\rho}-\frac{2}{\tilde{r}}\right]-\frac{30c_{+-}}{\tilde{r}^8}-\frac{56d_{+-}}{\tilde{r}^{10}}\right]\right.$$
$$+\frac{2b'}{\rho}\exp\left[-\frac{\tilde{R}}{\rho}\right]\left[\frac{1}{\rho}-\frac{3}{\tilde{R}}\right]+\frac{2}{\rho}A(r)\left[\frac{1}{3\rho}-\frac{1}{\tilde{r}}\right]$$
$$-\left\{\frac{1}{3}\left[\frac{b}{\rho}\exp\left[-\frac{\tilde{r}}{\rho}\right]\left[\frac{1}{\rho}+\frac{1}{\tilde{r}}\right]-\frac{48c_{+-}}{\tilde{r}^8}-\frac{80d_{+-}}{\tilde{r}^{10}}\right]+\frac{A(r)}{\rho}\left[\frac{2}{3\rho}+\frac{1}{\tilde{r}}\right]-\frac{(2.519Z^2e^2)3^{3/2}}{16\tilde{r}^3}\right\}^2$$

$$\times\Bigg\{\frac{1}{3}\left[\frac{b}{\rho}\exp\left[-\frac{\tilde r}{\rho}\right]\left[\frac{1}{\rho}-\frac{2}{\tilde r}\right]-\frac{30c_{+-}}{\tilde r^{8}}-\frac{56d_{+-}}{\tilde r^{10}}\right]+\frac{2A(r)}{\rho}\left[\frac{1}{3\rho}-\frac{1}{\tilde r}\right]$$

$$-\frac{(\pi Z^2e^2)3^{3/2}}{48\tilde r^{3}}\Bigg\}^{-1}\Bigg]\Bigg[-0.0169\frac{Z^2e^2}{\tilde r^{4}}+\frac{3.1579ea}{v_0\rho\tilde r^{2}}(d_+-d_-)\left[\frac{1}{\rho}+\frac{1}{\tilde r}\right]\exp\left[-\frac{\tilde r}{\rho}\right], \tag{35c}$$

where $A(r)=[A(1)+A(2)]\exp(-2\tilde r/\rho)$ and the other parameters have been defined earlier. It is found that the quadrupolar deformation contributes only to C_{44} while the scalar deformation affects all the three elastic constants. The contribution of quadrupolar deformation to internal strain has been neglected. The values obtained for the individual elastic constants and the cohesive energy for the three crystals are given in Table IV.

IV. LATTICE DYNAMICS AND DIELECTRIC PROPERTIES

The dynamical equations are obtained by expanding Eq. (4) about the equilibrium configuration and retaining terms up to second order in displacement, u_{ij} and/or dipole moments μ_i. Then using Eq. (33) the total dynamical equations are given by

$$[(\underline{Z}+\underline{D})\underline{C}(\underline{Z}+\underline{D}^T)+\underline{R}'+\underline{T}+\underline{Q}^{(1)}]\underline{U}+[(\underline{Z}+\underline{D})\underline{C}-\underline{R}'\underline{y}^{-1}+\underline{Q}^{(2)}]\underline{\mu}=mw^2\underline{U}\ , \tag{36a}$$

$$[-\underline{C}^T(\underline{Z}+\underline{D}^T)-\underline{y}^{-1}(\underline{R}')^T+(\underline{Q}^{(2)})^T]\underline{U}+[\underline{C}+\underline{\alpha}^{-1}\underline{y}^{-1}\underline{R}'\underline{y}^{-1}]\underline{\mu}=0\ , \tag{36b}$$

where $\vec U=(\vec U_1,\vec U_2)$ and $\vec\mu=(\vec\mu_1,\vec\mu_2)$ are the amplitudes of the ionic displacement and dipole fluctuation vectors [$\vec\mu$ is not to be confused with $\vec\mu_i^{\,c}$ in Eq. (4) which is the total moment], respectively, and $\underline{Z}$, $\underline{y}$, $\underline{m}$, $\underline{\alpha}$, are the usual 6×6 matrices—$\underline{C}$,$\underline{D}$, and $\underline{Q}$ are the 6×6 matrices corresponding to the Coulomb, deformation dipole, and quadrupole, respectively, and $\underline{R}'$ is given by

$$\underline{R}'=\underline{R}+\underline{H}+\underline{V}\ , \tag{37}$$

where $\underline{R}$, $\underline{H}$, and $\underline{V}$ represent the matrices for nearest-neighbor overlap interaction, the overlap interaction between the anions and the van der Waals interaction. $\underline{T}$ matrix represents scalar deformation. The equations (36) are now solved for the three symmetry directions to yield the eigenfrequencies for the three crystals and the results are shown in Figs. 2–4.

Next we calculate the macroscopic dielectric quantities. The dielectric equations are easily obtained from the dynamical equations (36) in the limit $q\to0$ which are given below: The force equations are

$$\begin{aligned}m_1\ddot{\vec u}_1&=(\underline{Z}_1-\underline{D}_0)\vec E_{\text{eff}}-\underline{R}_0(\vec u_1-\vec u_2)-(\underline{R}_0\underline{y}^{-1}+\underline{Q}^D)\vec\mu^{\,c}\ ,\\ m_2\ddot{\vec u}_2&=(\underline{Z}_2+\underline{D}_0)\vec E_{\text{eff}}-\underline{R}_0(\vec u_2-\vec u_1)+(\underline{R}_0\underline{y}^{-1}+\underline{Q}^D)\vec\mu^{\,c}\ ,\end{aligned} \tag{38}$$

and the adiabatic equation is

TABLE IV. Cohesive energy, elastic and dielectric constants of the Cu halides.

	C_{11} (10^{12} dyn/cm^2)		C_{12} (10^{12} dyn/cm^2)		C_{44} (10^{12} dyn/cm^2)		Cohesive energy (10^{-12} erg)		ϵ_0		ϵ_∞	
Crystal	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
CuI	0.497	0.451[a]	0.390	0.307[a]	0.170	0.182[a]	−13.58	−14.81[c]	10.276	9.12[d]	5.969	5.48[d]
CuBr	0.453	0.458[a]	0.373	0.354[a]	0.157	0.139[a]	−14.11	−15.01[c]	6.232	6.29[f]	4.41	4.06[f]
CuCl	0.405	0.522[b]	0.330	0.428[b]	0.170	0.133[b]	−14.45	−15.42[c]	6.02	5.95[e]	3.65	3.61[e]

[a] Reference 32.
[b] Reference 3.
[c] Reference 33.
[d] Reference 15.
[e] Reference 34.
[f] Reference 35.

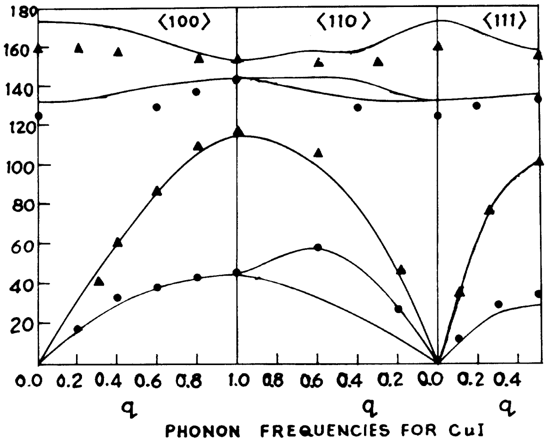

FIG. 2. Phonon dispersion curves of CuI at room temperature. Experimental points are taken from Ref. 36.

$$0=-\underline{y}\vec{\mathrm{E}}_{\mathrm{eff}}+(\underline{y}\underline{\alpha}^{-1}+\underline{R}_0\underline{y}^{-1})\vec{\mu}^{c}$$

$$-(\underline{R}_0+\underline{y}\underline{Q}^{D})(\vec{\mathrm{u}}_2-\vec{\mathrm{u}}_1)\ , \qquad (39)$$

where m_1 and m_2 are the masses, and u_1 and u_2 are the displacements of the positive and negative ions, respectively. R_0 is defined as $-R'|_{q=0}$. Following Hardy and Karo the deformation dipole matrix $D(ij)$ is written as

$$\mu_i^d=\sum_j D(j,i)u_j$$

$$=-\sum_j{}' m_i(r_{ij})\frac{\vec{\mathrm{r}}_{ij}}{r_{ij}}\ , \qquad (40)$$

where $m=c\exp(-r/\rho')$ and $D_{\vec{0}}$ in Eqs. (38) and (39) is the value of D at $q\rightarrow 0$. $\vec{\mathrm{E}}_{\mathrm{eff}}$ is the effective electric field at the ion site and

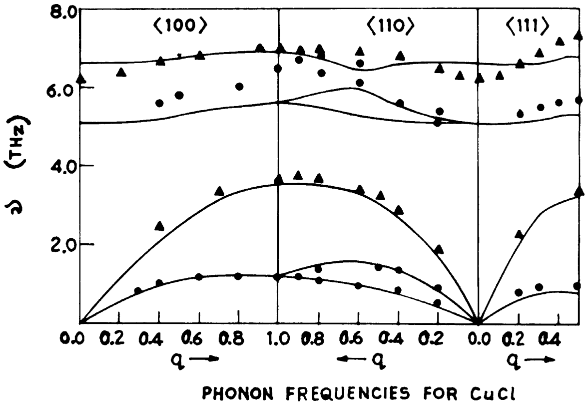

FIG. 3. Phonon dispersion curves of CuCl at 4.2 K. Experimental points are taken from Ref. 12.

$$Q^D=(d_+ + d_-)q'^{s}_{\alpha\beta\gamma}\psi_{\alpha\beta\delta} \qquad (41)$$

is the quadrupolar contribution to the dielectric properties. This term vanishes for cubic crystals with a center of symmetry. Equations (38) and (39) together with the Huang relations,[24] give the three macroscopic dielectric properties, namely the high- and the low-frequency dielectric constants and the Raman frequency. The values of these quantities for the three copper halides are given in Table IV.

The expressions for the high- and low-frequency dielectric constants ϵ_∞ and ϵ_0 in terms of the model parameters, are

$$\epsilon_\infty=1+4\pi b_{22}\ ,$$

$$\epsilon_0=\epsilon_\infty-\frac{4\pi b_{12}^2}{b_{11}}\ , \qquad (42)$$

where the Huang coefficients[24] b_{11}, b_{12}, and b_{22} are given by

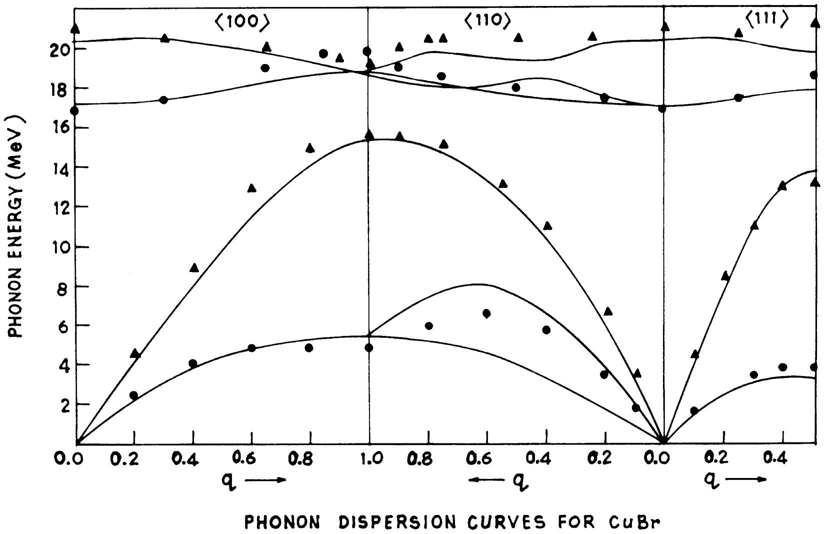

FIG. 4. Phonon dispersion curves of CuBr at 77 K. Experimental points are taken from Ref. 13.

$$b_{11}=-\frac{1}{\bar{m}}\left[C_1-\frac{\frac{4\pi}{3v_0}(Z_1'e)^2}{1-\frac{4\pi}{3v_0}\alpha_e}\right], \tag{43a}$$

$$b_{12}=\frac{Z_1'e}{(\bar{m}v_0)^{1/2}}\frac{1}{1-\frac{4\pi}{3v_0}\alpha_e}, \tag{43b}$$

and

$$b_{22}=\frac{\alpha_e}{v_0}\frac{1}{1-\frac{4\pi}{3v_0}\alpha_e}, \tag{43c}$$

where

$$\frac{1}{\alpha_e}=\frac{1}{\alpha}+\frac{R_0}{y^2e^2},$$

$$Z_1'e=e(Z_1-D_0)-\frac{R_0\alpha_e}{ye}-\alpha_eQ^D,$$

and

$$C_1=R_0-\frac{R_0^2\alpha_e}{y^2e^2}-(2R_0+yeQ^D)\frac{Q^D\alpha_e}{ye}.$$

Here v_0 is the unit cell volume, Z_1 is the charge of the positive ion, and $\bar{m}=(m_1m_2)/(m_1+m_2)$ is the reduced mass.

V. DISCUSSION

Examining the results given in Table IV and in Figs. 2–4, we find that the present phenomenological model based on the energy expression (4), is capable of providing a broad overall description of the lattice mechanical properties of the three Cu halides with a single set of parameters for each crystal.

Next we discuss the role of the various types of charge cloud deformation envisioned in the present model in the description of the properties of different crystals. It is well known that the scalar, dipolar, and quadrupolar deformations of the charge cloud of an ion depend upon the details of the ground-state wave functions of the ion and the modification it undergoes in a crystal environment, which is, of course, difficult to judge beforehand. But the results of the present calculation indicate certain trends. An inspection of Table III shows that the parameter values increase or decrease progressively from CuI, CuBr to CuCl. The second-neighbor interaction is particularly important for CuI but its importance decreases progressively from CuBr to CuCl. This is also evident from the value of the parameter b' in Table III. The effect of scalar deformation, in particular for the charge cloud of the copper ion, increases progressively from CuI to CuCl and its contribution to some phonon frequencies also increases in this order. The contribution of this deformation to elastic constants is large, but its contribution to the cohesive energy and the dielectric properties is quite small in all three crystals. On the other hand, the effect of the quadrupolar deformation increases from CuCl to CuI. In particular, the ⟨100⟩ and ⟨111⟩ zone boundary frequencies are affected most. In CuBr and CuCl, the quadrupolar deformation affects the LO, LA, and TA branches in the ⟨100⟩ and ⟨111⟩ directions but the strongest effect is seen in the ⟨100⟩ zone boundary frequencies in the case of CuI, where the effect is about 15%. The two types of short-range dipolar deformations considered are found to be essential for a consistent description of the dielectric properties and the phonon dispersion relation in all the Cu halides. The deformation dipole has considerable effect on the TA and TO branches along ⟨100⟩ and ⟨110⟩ directions and on the LA branch along ⟨111⟩ direction—e.g., in CuBr its effect is about 64% at the ⟨100⟩ TA zone boundary and 20% at the ⟨111⟩ LA zone boundary. Without the distortion dipole the TA frequencies along all three symmetry directions turn imaginary. In all the calculations we have kept the ionic charge fixed at unity, which appears to be too stringent. Slight lowering of the same might further improve the agreement for the phonon dispersion relation, while not deviating too much from the measured cohesive energy.

Before we conclude let us discuss some of the limitations of the present calculation. The present approach is not a microscopic one. What we have attempted is to adduce only some plausibility justification for the general energy expression that we use. Naturally the procedure has the usual limitations associated with a phenomenological approach. A comparative study of the result of the three crystals approximately indicates that the adequacy of description in the framework of the present model, gradually decreases as we pass from CuI to CuCl. Although we do not find any large-scale discrepancy in any property as in previous calculations, there is a definite trend in discrepancy in the ⟨100⟩ zone boundary frequency TO, which gradually increases from CuI and becomes about 15% low for CuCl. Again, the overall agreement of the elastic constants for the CuCl crystal is not as satisfactory as that of the other two crystals. All these tend to show that although we have obtained an overall description, there is some definite effect not included in the present model, which is at least essential for the CuCl crystal. One such may be the inclusion of the effect of the *d*-*s*-*p* hybridization of the *d* states of the copper ion. This may be plausible since the decrease in distance between the copper ions as one passes down the series from CuI to CuCl may increase the hybridization which will contribute an additional term to the energy expression (4). This contribution may be calculated if we start from the hybridized orbitals instead of the free ion orbitals as in Eq. (2). This might be a possible direction of refinement at the microscopic level. A proper understanding of the physical processes in these solids requires a microscopic calculation from which we are still far off and the present calculation only provides a suitable interpolating phenomenological model with its several inherent weakness and inadequacies. What has been concretely achieved in the present investigation over the existing calculations is that we have been able to obtain an overall description of the different lattice mechanical properties of the three copper halides with a set of physically meaningful parameters for each crystal.

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APPENDIX A

We briefly discuss the method of evaluation of the long-range lattice sums that occur in the elastic constants and the lattice dynamics. Since the results obtained are of general interest and do not refer to any particular interaction we tabulate the sums for the symmetry points which may be used for various purposes. The lattice sums required for the calculation of the terms in curly brackets, i.e., for the elastic constants, are evaluated by the method of Born and co-workers[29,30] and are given in Table I; l_1, l_2, l_3 denote the coordinates of the lattice points of a zinc-blende structure crystal. $(\alpha_1,\alpha_2,\alpha_3)$ is taken as (π,π,π) to take account for the alteration of sign of the positive and the negative ions. The sums have been evaluated assuming k to be positive and so when k is negative, the sum is to be taken with a negative sign.

The long-range periodic lattice sums between the unlike particles in a zinc-blende lattice that appear in the lattice dynamics cannot be evaluated by Born's method which is applicable only to a lattice with a center of symmetry. Chatterjee *et al.*[31] have developed a modification of Born's method by which the lattice sums for unlike particles given in Table II have been evaluated. The like particle sums are given in Ref. 22.

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[1] J. A. Van Vetchen, Phys. Rev. 187, 1007 (1969).

[2] J. B. Boyce and B. A. Huberman, Phys. Rep. 51, 189 (1979).

[3] T. H. K. Barron, J. A. Birch, and G. K. White, J. Phys. C 10, 1617 (1977).

[4] H. P. Schaake, AFCRL Report No. 69-0583 (unpublished) quoted by N. Plendl and L. C. Mansur, Appl. Opt. 11, 1194 (1972).

[5] A. P. Rusakov, Phys. Status Solidi B 72, 503 (1975).

[6] C. W. Chu, A. P. Rusakov, S. Huang, S. Early, T. H. Geballe, and C. Y. Huang, Phys. Rev. B 18, 2116 (1978).

[7] A. Ghosh and A. N. Basu, Phys. Rev. B 14, 4616 (1976).

[8] A. Ghosh, A. N. Basu, and S. Sengupta, Proc. R. Soc. (London) Ser. A 340, 199 (1974).

[9] A. Ghosh and A. N. Basu, Phys. Rev. B 17, 4558 (1978).

[10] S. Ghosh, A. N. Basu, and S. Sengupta, Phys. Rev. B 23, 1818 (1981).

[11] S. Ghosh, A. N. Basu, and S. Sengupta, Phys. Rev. B 25, 5953 (1982).

[12] B. Prevot, B. Hennion, and B. Dorner, J. Phys. C 10, 3999 (1977).

[13] S. Hoshino, Y. Fujii, J. Harda, and J. D. Axe, J. Phys. Soc. Jpn. 41, 965 (1976).

[14] Z. Vardeny, G. Gilat, and A. Pasternak, Phys. Rev. B 18, 4487 (1978).

[15] K. Kunc, M. Balakanski, and M. A. Nusimovici, Phys. Status Solidi B 72, 229 (1975).

[16] Z. Vardeny, G. Gilat, and A. Pasternak, Phys. Rev. B 11, 5175 (1975).

[17] S. S. Jaswal, Solid State Commun. 27, 969 (1978).

[18] L. K. Banerjee, A. N. Basu, and S. Sengupta, Phys. Rev. B 26, 1018 (1982).

[19] J. R. Hardy and A. M. Karo, Philos. Mag. 5, 859 (1960).

[20] W. Cochran, Crit. Rev. Solid State Sci. 2, 1 (1971).

[21] W. G. Kleppmann and W. Weber, Phys. Rev. B 20, 1669 (1979).

[22] S. Ghosh, A. N. Basu, and S. Sengupta, Phys. Status Solidi B 103, 595 (1981).

[23] S. Ghosh, A. N. Basu, and S. Sengupta, Phys. Status Solidi B 94, 673 (1979).

[24] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954).

[25] A. N. Basu, D. Roy, and S. Sengupta, Phys. Status Solidi A 23, 11 (1974).

[26] S. Sarkar and S. K. Chakraborti, Z. Phys. B 22, 309 (1975).

[27] V. Nusslein and U. Schroder, Phys. Status Solidi 21, 309 (1967).

[28] G. Leibfried and W. Ludwig, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1961), Vol. 12, p. 275.

[29] M. Born and R. D. Mishra, Proc. Cambridge Phil. Soc. 36, 466 (1940).

[30] M. Born and M. Bradburn, Proc. Cambridge Phil. Soc. 39, 104 (1943).

[31] S. Chatterjee, S. Ghosh, and A. N. Basu, Phys. Status Solidi B 106, 693 (1981).

[32] R. C. Hanson, J. R. Hallberg, and C. Schwab, Appl. Phys. Lett. 21, 490 (1972).

[33] C. Kittel, *Introduction to Solid State Physics* (Eastern Private, New Delhi, 1971).

[34] J. E. Potts, R. C. Hanson, C. T. Walker, and C. Schwab, Phys. Rev. B 9, 2711 (1974).

[35] E. H. Turner, I. P. Kaminow, and C. Schwab, Phys. Rev. B 9, 2524 (1974).

[36] B. Hennion, F. Moussa, B. Prevot, C. Carabatos, and C. Schwab, Phys. Rev. Lett. 28, 964 (1972).