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Deformable shell-model calculation of the lattice statics and dynamics of the CsBr crystal

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In this report we present a simple statistical-model derivation of the three-body interaction envisaged in the deformable-shell model developed by Basu and Sengupta. Next the model is applied to a unified study of the lattice statics and dynamics of the CsBr crystal, the same set of parameters being used throughout. Among the alkali halide crystals, the cesium group of halides are distinguished from the rest by two characteristic problems of the their own—one related to the stability of the static lattice structure and the other concerning the correlation of the dielectric properties and the dispersion of phonons. The results of the present calculation show that this simple model gives a good description of the lattice mechanics of the CsBr crystal in all its totality and the source of improvement for the remaining discrepancy is suggested.

I. INTRODUCTION

In a previous paper[1] we have made an extensive investigation on the dynamic properties of crystals having NaCl structure on the basis of the deformable-shell model developed by Basu and Sengupta.[2] The results obtained have been quite satisfactory and the model appears to be empirically verified. Hence in the present work we have attempted a justification of the three-body interaction implied by the model from a simple statistical-model consideration. Apart from the present model there are other models, namely, the modified rigid-ion model,[3] the breathing-shell model,[4] and the model of Singh and Verma,[5] which also more or less correctly reproduces the phonon data of the alkali halides with NaCl structure. But there have been only a few attempts to correlate simultaneously the static and the dynamic aspects of alkali halides in the framework of a single model. Recently we have considered such a unified study[6] of the NaF crystal in the framework of the deformable-shell model and the results obtained have been quite encouraging. It cannot, however, be denied that the validity of the above-mentioned models is more rigorously tested, if they are applied to a comprehensive calculation embodying both the static and the dynamic properties of a solid. In a recent review article[7] we have intercompared these different lattice-dynamical models and have noted that all the above-mentioned models have the potentiality of such an application. One of the motivations of the present work is to attempt such a calculation for the CsBr crystal.

The cesium group of halides are distinguished from the rest of alkali halides by two characteristic problems of their own. One is concerned with the stability of these crystals. It has been known for a long time that no reasonable two-body central interaction[8,9] can predict the correct lattice static structure for the three crystals, CsBr, CsCl, and CsI. Many intensive investigations[10-12] of this problem have been carried out in recent times and most of the work leads us to conclude that the many-body interaction in some form might be responsible for the static lattice structure of these three crystals. Sarkar and Sengupta[13] have obtained the correct structure for them with a three-body potential arising out of the deformation of the charge cloud of an ion.

The second one is concerned with the dielectric behavior of these crystals. The dispersion of phonons and the dielectric constants are quite successfully correlated in the above-mentioned polarizable models for alkali halides with NaCl structure. Unlike other alkali halides, for this triplet of cesium halides the dielectric properties and the dispersion of phonons are correlated only inexactly in the present polarizable models. For example, in order to obtain a reasonable fit with the phonon frequencies in the symmetry directions for the CsBr crystal on the breathing-shell model[23] the static and the high-frequency dielectric constants have to be lowered by 40 and 45%, respectively. Moreover, in this calculation the value of the ionic charge used is 0.85 which means that if one calculates the cohesive energy of this crystal it will be considerably lowered. On the other hand, the value of cohesive energy can be improved only at the expense of agreement for the phonon data.

In the present work we have attempted a calculation of the major aspects of the lattice statics and the dynamics of the CsBr crystal with the deformable-shell model. We have tried to correlate the following specific properties: the cohesive energy, the static-lattice structure, the second-order harmonic elastic constants, and the dispersion of phonons in the symmetry directions, and the dielectric constants. We have consistently used the same set of parameters in all the calculations. In Sec. II we consider the derivation of the three-body interaction and the method of calculation.

II. THREE-BODY INTERACTION AND METHOD OF CALCULATION

Basu and Sengupta[2, 14] have considered the effect of an isotropic scalar deformation of the electron charge cloud on the dynamics of a crystal. They have derived an expression for the force constants that arises from the deformation and demonstrated that the force constant is due to an effective three-body interaction between the ions in a lattice. Sarkar and Sengupta[13] suggested empirically a form for this three-body interaction which generates the same set of force constants. In the following we give a justification of the form from certain simple consideration.

In the present analysis we shall follow the Thomas–Fermi-Dirac statistical method which has been used by Jensen and others[15] to study the properties of ionic crystals. In the statistical method, instead of wave functions the attention is focused on the charge density around each ion. Let ρ_{0k} be the equilibrium density function around an isolated k ion. The total energy of the ion, E_{0k}, may be obtained from an energy-density function ϵ such that

$$E_{0k}=\int \epsilon(\rho_{0k})\,d\vec{r}\ . \tag{1}$$

The energy density here includes contributions from the (i) classical Coulomb energy, (ii) the zero-point kinetic energy, and (iii) the exchange energy. The expression for $\epsilon(\rho)$ is given by Born and Huang.[16] The equilibrium density function ρ_{0k} as a function of $\vec{r}$ is obtained from the condition of minimum energy.

When the ions are brought together to form a crystal, the total energy of the crystal will be the sum of the individual energies of the ions plus the additional Coulomb energy of the ions, provided there is no overlap in the charge density of ions. If overlap occurs, one may put the density in the overlap region to be the sum of the densities of the individual ions at that region. Since $\epsilon(\rho)$ is not a linear function of ρ, this lends extra energy of interaction between the ions, and gives rise to the well-known repulsive overlap interaction. In the treatment of the overlap interaction by Jensen and others,[15] it is assumed that even when the ions are brought together, their charge densities remain unaltered and correspond to the values obtained for the isolated ions. Thus the effect of the deformation of the charge cloud is neglected.

We shall assume that in the presence of other ions the charge-density function of the lk ion is no longer given by ρ_{0k}. Instead it is given by

$$\rho_{lk}=\rho_{0k}+\delta\rho_{lk}\ , \tag{2}$$

where $\delta\rho_{lk}$ is the deformation of the charge cloud. It may be noted that we are not assuming here that all the ions are occupying the normal lattice sites. They may have arbitrary displacements from their normal position. If we expand the energy density function $\epsilon(\rho_{lk})$ about ρ_{0k} and retain second-order terms only, then

$$\epsilon(\rho_{lk})=\epsilon(\rho_{0k})+\delta\rho_{lk}\,\epsilon'(\rho_{0k})+\tfrac{1}{2}\delta\rho_{lk}^2\,\epsilon''(\rho_{0k}). \tag{3}$$

When many ions are present, the energy density function may be written

$$\epsilon(\rho)=\epsilon\left(\sum_{lk}\rho_{lk}\right)\ , \tag{4}$$

where $\sum_{lk}\rho_{lk}$ is the resultant density at any point. Separating the overlap term we may write

$$\epsilon(\rho)=\sum_{lk}\epsilon(\rho_{lk})+\epsilon_{0l}\ , \tag{5}$$

where ϵ_{0l} is the overlap energy density considered by Jensen. In the present treatment we neglect the effect of deformation on the overlap energy density. Substituting for $\epsilon(\rho_{lk})$ from Eq. (3), we get from Eq. (5):

$$\epsilon(\rho)=\sum_{lk}\epsilon(\rho_{0k})+\sum_{lk}\delta\rho_{lk}\,\epsilon'(\rho_{0k})+\frac{1}{2}\sum_{lk}\delta\rho_{lk}^2\,\epsilon''(\rho_{0k})+\epsilon_{0l}\ . \tag{6}$$

So far, we have not specified the nature of the deformation function, $\delta\rho_{lk}$. It has been shown by Basu and Sengupta[14] that, in general, we can separate $\delta\rho_{lk}$ in terms of spherical harmonics as follows:

$$\delta\rho_{lk}=f_0(r)+\sum_m f_{1m}(\vec{r})Y_{1m}(\theta,\varphi)+\sum_m f_{2m}(\vec{r})\,Y_{2m}(\theta,\varphi)\ , \tag{7}$$

the vector $\vec{r}$ being measured from the nucleus of the ion. The first term gives the isotropic scalar deformation, the second one a dipole deformation, and the third one a quadrupolar deformation. We confine our attention to the first term of the series. The effect of the second term is adequately incorporated in the framework of the shell model by Woods *et al.*[17], while the third term is neglected. To simplify matters we further assume that the deformation is defined by a single parameter a_{lk}. For small values of the deformation parameter, a_{lk} we may write

$$\delta\rho_{lk} = a_{lk} f_k , \tag{8}$$

where f_k is some isotropic function, the same for all ions of type k. For the total energy of the system we now get

$$E = \int \epsilon(\rho)\, d\vec{r} = \sum_{lk} E_{0k} + E_{0l} + \sum_{lk} a_{lk} G_k + \frac{1}{2}\sum_{lk} a_{lk}^2 F_k , \tag{9}$$

where

$$F_k = \int f_k^2 \epsilon''(\rho_{0k}) d\vec{r} \quad \text{and} \quad G_k = \int f_k \epsilon'(\rho_{0k}) d\vec{r} ,$$

and E_{0l} is the total overlap energy. We shall assume that the deformation of the lk ion is primarily due to overlap of those ions which are nearest neighbors of the lk ion. Precisely we put

$$a_{lk} = \sum_{\substack{l'k' \\ (\text{nn of } lk)}} B_k S^2(lk, l'k') , \tag{10}$$

where B_k is some constant characteristic of the k-ion, and $S(lk, l'k')$ is the overlap integral between the lk and $l'k'$ ions. To make this assumption consistent with that of Basu and Sengupta,[14] without much error, we may take that $S^2(lk, l'k')$ is proportional to the overlap potential $\phi(r(lk, l'k'))$. It may be noted that the deformation parameter, a_{lk} defined here is different from a_{lk} in Basu and Sengupta. In the latter case the deformation is defined with respect to the charge cloud of ions occupying the equilibrium positions in the lattice, whereas in the present case the deformation is defined with respect to the charge cloud around a free ion.

Substituting Eq. (10) in Eq. (9), we get

$$E = \sum_{lk} E_{0k} + E_{0l} + \sum_{lk} \sum_{\substack{l'k' \\ (\text{nn of } lk)}} G_k B_k S^2(lk, l'k')$$
$$+ \frac{1}{2}\sum_{lk} \sum_{\substack{l'k' \\ (\text{nn of } lk)}} F_k B_k^2 S^4(lk, l'k')$$
$$+ \frac{1}{2}\sum_{lk} \sum_{\substack{l'k', l''k'' \\ (\text{nn of } lk)}} F_k B_k^2 S^2(lk, l'k') S^2(lk, l''k''). \tag{11}$$

The third and fourth terms in Eq. (11) are the contribution from an effective two-body interaction and may be merged with the overlap energy. The fifth term is the contribution from an effective three-body interaction. This analysis shows that there is an interaction energy between $l'k'$ and $l''k''$ ions generated by the presence of the common nearest-neighbor (cnn) lk ion. If we now replace the overlap integral in Eq. (11) by the two-body overlap interaction, $\phi(r) = be^{-r/\rho}$, then we get the three-body interaction (Sarkar and Sengupta[13])

$$E_3 = \frac{1}{2} \sum_{l'k', l''k''} \sum_{\substack{lk \\ (\text{cnn of } l'k' \text{ and } l''k'')}} A(k) \exp\left(-\frac{r(lk, l'k') + r(lk, l''k'')}{\rho}\right) , \tag{12}$$

where $A(k)$ is some constant which measures the deformability of the k ion. Here we have assumed that both k and k' are the same type of ions, so that only one value of ρ is involved.

Here it is important to note that we do not treat the deformability as an additional independent degree of freedom whose value is determined by an adiabatic equation as in the breathing-shell model.[4] If this were so as in the breathing-shell model, it would immediately restrict deformability and hence $A(k)$ to values which are positive definite. Our assumption in Eq. (10) is thus crucial and effectively states that the deformation is uniquely determined by the instantaneous ionic position coordinates. There is no restriction on $A(k)$ to be positive.

In the present model the equilibrium condition is affected by minimizing the total static lattice energy and this is why we have used the harmonic value of the nearest-neighbor distance and the harmonic value of the cohesive energy in the determination of the parameters.

In this treatment of the problem of the isotropic deformation of the charge cloud we have proceeded in a phenomenological way and used the somewhat crude statistical model. It is certainly desirable to treat the problem of deformation in a more fundamental way. Most of the calculations of the energy of a crystal from a fundamental quantum-mechanical standpoint, such as that of Lowdin[18] and Lundqvist[19] and others which are based on a Heitler-London approximation, are confined to first-order effects, where the deformation of the charge cloud is neglected. Recently, several authors[20-22] have tried to develop a microscopic theory of lattice dynamics which includes deformation. But in all these calculations, the attention is confined to the dipole deformation alone. In absence of a more refined calculation the above may be considered to be a plausibility argument analysis in favor of Eq. (12). It may, however, be noted that Eq. (12) represents a very simple and tractable form for the three-body interaction.

Next in order to compute the properties of the

TABLE I. Values of input data and parameters.

Input data	Parameters
$\tilde{\beta}^{-1}=0.5717\times 10^{12}$ dyn/cm^2 [a]	$b=2.9126\times 10^{-8}$ ergs.
$\vec{r}=3.6762$ Å [a]	$\rho=0.3075\times 10^{-8}$ cm
$\tilde{\Phi}=151.8$ kcal/mol. [b]	$A(1)=4.012\times 10^{-5}$ dyn/cm
$\epsilon_0=6.45$ [c]	$A(2)=-7.422\times 10^{-5}$
$\epsilon_\infty=2.18$ [c]	$Y=8.3804$
$\omega_{LA}=1.44\times 10^{13}$ [c]	$K=230.9\times 10^4$ dyn/cm

[a] See Ref. 26.

[b] See Ref. 11. The value quoted in this reference has been corrected for zero point energy as estimated by Seitz.

[c] See Ref. 23.

CsBr crystal the interactions retained are the Coulomb interaction, the repulsive interaction between nearest neighbors only, the Van der Waals interaction, and the three-body interaction given by Eq. (12). The dipole forces are calculated in the framework of a polarizable negative ion shell model.[17]

Assuming the ionic charge to be unity the six parameters of the model, namely, b, ρ (short-range repulsive parameters), Y (negative ion shell charge), K(core-shell spring constant), and $A(1)$ and $A(2)$ (many-body interaction parameters) have been calculated from the harmonic value of the cohesive energy, the harmonic bulk modulus, the LO-phonon frequency at $\vec{q}=(\pi/a)(1,0,0)$ direction, and the static and high-frequency dielectric constants, ϵ_0 and ϵ_∞. The expressions for the cohesive energy and the elastic constants and the force-constants corresponding to the three-body interaction are evaluated in the usual procedure. The values of the parameters together with the input data are given in Table I. While calculating the dispersion relation we use the quasiharmonic approximation. The values of r, ϵ_0, ϵ_∞ used therefore correspond to the temperature of the phonon measurement, namely, 80 °K (for details see Ref. 6).

III. RESULTS AND DISCUSSION

First of all we have considered the stability of the static lattice structure of the crystal. The detailed method of the calculation is given in Refs. 6 and 13. In Table II we have compared the value of the harmonic cohesive energy of the real lattice with that in the hypothetical structure (NaCl structure in this case) and it is seen that the correct structure is predicted. With the same set of parameters the second-order harmonic elastic constants have also been calculated and compared with experiment. The agreement is found to be quite satisfactory. The results also show that the presence of the explicit many-body interaction takes account of the breakdown of the Cauchy relation for this crystal.

Next we have calculated the phonon frequencies in the symmetry directions with the same set of parameters used for the evaluation of the static properties. The dynamical equations are the same as given in Ref. 1. The calculated and experimental frequencies[23] are displayed in Fig. 1.

The results of the present calculation show that a satisfactory description of both the static and dynamic aspects of the CsBr crystal is obtainable in the deformable shell model. However, a close examination of Fig. 1 will reveal that there exist certain discrepancies (~10%) in the LO branches of the dispersion curves apart from some minor discrepancies in the acoustic branches. The LA frequencies in the [100] and [110] directions may be somewhat improved by the inclusion of the short-range potential beyond nearest neighbors. But the overall discrepancy seems to be arising partly out of the neglect of the polarizability of the positive ion. But it is apparent from the works of Rolandson *et al.*[23] that even this inclusion is unable to

TABLE II. Relative stability and second-order harmonic elastic constants.

Structure	Harmonic nn distance	Cohesive energy	Phase transition pressure
NaCl [a]	3.6085 Å	151.3 kcal/mol.	−1.454 kbar
CsCl [b]	3.6762 Å	151.8 kcal/mol.	

Elastic constants	Calc. (10^{12} dyn/cm^2)	Expt. (10^{12} dyn/cm^2)
$\tilde{C}_{11}$	0.3471	0.3445
$\tilde{C}_{12}$	0.1014	0.1036
$\tilde{C}_{44}$	0.1215	0.1042

[a] Hypothetical structure.

[b] Stable structure.

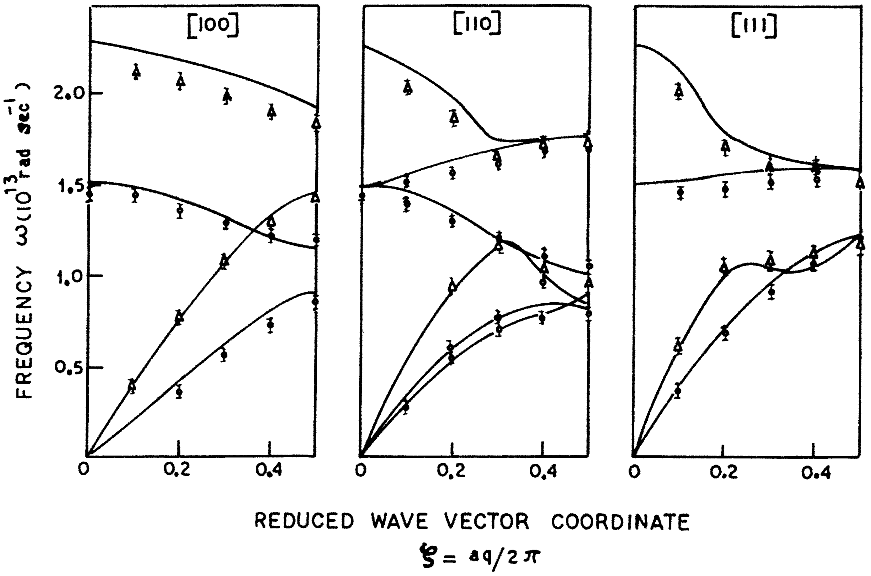

FIG. 1. Phonon dispersion curves in the symmetry directions; solid line represents the theoretical curves. Experimental points are taken from Ref. 23.

correlate dielectric properties and the phonon dispersion relation as discussed earlier. There are two other recent calculations on the phonon dispersion of the crystal by Lal *et al.*[24] and Agrawal *et al.*[25] In the calculation by Agrawal *et al.* the ionic charge has been significantly lowered to improve agreement for phonon dispersion, whereas in that of Lal *et al.* the full ionic charge has been retained at the cost of agreement for phonon data which is worse than the present calculation. Moreover, the present calculation alone predicts the correct structure of the crystal in addition to a reasonable description of the other properties in the framework of a single model, and using the same set of parameters.

From the present investigation and the above discussions it is quite clear that no dipolar force model is capable of rendering a consistent description of the dielectric properties and the dispersion of phonons. In view of this it seems reasonable to conclude that the remaining discrepancy with experiment in the present model might be due to the neglect of the third term in Eq. (7), i.e., the quadrupolar deformation of the charge cloud.

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