Model calculation of the pressure derivative of the low-frequency dielectric constant of alkali halide crystals

Lalit K. Banerjee and A. N. Basu

Physics Department, Jadavpur University, Calcutta-700032

S. Sengupta

Solid State Physics Research Centre, Physics Department Presidency College, Calcutta-700073

The mechanism of polarization of insulators in a static electric field is still not clearly understood. The current situation presents an anomaly. The model which describes the high-frequency dielectric behavior quite well is found to be inadequate for the static case. In fact, with the same set of parameters within any single phenomenological model, it has not been possible to describe satisfactorily both the dielectric constants and their pressure derivatives. In search of a suitable model which can achieve this we have, in the present work, tried to analyze the mechanism of polarization from first principles. The interesting finding of this analysis is that there are two types of short-range polarization effects having entirely different origins: One of which (the second-order exchange interaction) contributes both to the static and high-frequency dielectric properties and the other (the first-order exchange interaction) to the static one only. We have suggested a model based on this analysis. The present calculation of the pressure derivative of the static dielectric constant of alkali halide crystals within a simplified version of this model together with our earlier calculation of the same for the high-frequency dielectric constant provides a fair overall description of the entire dielectric behavior of insulators. In addition, the present investigation also discusses the approximations which yield the well-known models for ionic solids which include polarization.

I. INTRODUCTION

The properties related to the high-frequency response of the electron system of insulators have been extensively studied both theoretically and experimentally. There has been quite significant advancement of our understanding about the details of the mechanism of electronic polarization in the case of the alkali halide crystals. In a previous paper[1] we have discussed at length the different theoretical models and indicated their success and limitations. The idea of an effective anion state in the crystal is used there to modify the shell-model dielectric theory[2], which, we have shown, accounts more or less satisfactorily for the behavior of the high-frequency dielectric constant and its variation with pressure. So it is expected that the same theory should describe the behavior of the system while responding to a static electric field, to be specific about the low-frequency dielectric constant and its variation with pressure. But it is not so. Moreover, it is to be noted that all the existing model calculations are inadequate if we demand a simultaneous description of the low- and high-

frequency dielectric behavior of the alkali halide crystals including their pressure variation. In addition, from a critical analysis[3] of the two Szigeti relations for the alkali halides on the basis of the existing models we have concluded that the shell model is good for some ionic crystals and for others the deformation dipole model[4] may be better. Further, the shell-model calculation of the pressure derivative of even the static dielectric constant alone is not satisfactory.[5]

The above discussion, apart from showing the anomalous situation, seems to indicate clearly the presence of some new effect which has been neglected in the pressure-derivative calculation of the low-frequency dielectric constants. And the effect appears to be such as to affect the static polarization mechanism and not to disturb the high-frequency one. For the high-frequency probe, like the electromagnetic wave, the electron system alone participates in the polarization mechanism of an ion and the modified shell-model dielectric theory[1] mentioned above seems to be adequate for it. In case of the static electric field both the electronic and ionic displacements are important. Hence it is

quite plausible that the finer details of the ionic response will be important for the low-frequency dielectric behavior of the insulators while it may not affect the high-frequency dielectric properties in any substantial way. In order to have a suitable model which will describe both the dielectric constants and their pressure derivatives within the framework of a single model we propose to analyze the energy expression of an assembly of ions that constitute an insulator with special emphasis on the terms that are responsible for the polarization effect. An interesting finding of this analysis is that there are two types of polarization mechanisms having entirely different origins; one affects both the dielectric constants and the other, which is related to the effective ionic charge, contributes only to the static dielectric constant. Unfortunately, the first-principles calculations become intractable after this and cannot be rigorously pushed to evaluate the properties in which we are interested. Based on this microscopic analysis we have suggested a model which incorporates both mechanisms. A simplified version of the model is employed to calculate the pressure derivative of the low-frequency dielectric constant of several alkali halide crystals. It is found that the present model offers a fair overall description of the dielectric behavior of the crystals in their entirety. The present analysis also provides insight into the polarization mechanisms envisaged in the current phenomenological models.[2,4]

In the following section we discuss the energy expression and identify the terms responsible for the polarization effect. In Sec. III we develop the model based on this analysis and deduce the dielectric equations within it. In Sec. IV we consider an application of the model to some alkali halide crystals. Section V discusses the results of our calculation.

II. ENERGY EXPRESSION
FOR AN ASSEMBLY OF IONS

The analysis we pursue in this section is due to Sengupta et al.[6] The model we shall discuss in the next section based on this analysis has certain distinct advantages over the pure phenomenological one in the sense that we need not have to introduce the crude classical notions such as shells, springs, etc., as in the well-known shell model. All interaction terms occurring in the final model will correspond to some definite microscopic origin. This approach is somewhat analogous to the analysis

advanced by Tolpygo[7] long before the advent of the polarizable models for ionic solids. In the following we shall emphasize the polarization part of the entire analysis.

Unlike Lowdin's treatment[8] we shall employ for the discussion of the energy expression a straightforward Heitler-London method of construction of the wave function first used for ionic crystals by Paul et al.[9] Denoting by the one electron wave function the ion at site G, where $v=G,i,\sigma$ (i and σ indicating the spatial and the spin quantum number, respectively), we construct the antisymmetric wave function for the crystal. We associate with every lattice site G a positive nucleus of charge $Z_G e$ and electronic charge, $n_G e$, and $\epsilon_G e = (Z_G - n_G)e$ is the net ionic charge at G. With an even number of electrons the electronic states are occupied including both spin states $\sigma = \pm 1$, the normalized antisymmetric wave function for the ion is given by

$$\phi_G = A_G \prod_{i\sigma} \phi_v ,\qquad(1)$$

where A_G is a normalized antisymmetric operator acting on the electrons of the G ion, Φ_G being the ground-state wave function. The antisymmetric ground-state wave function for the entire solid is given by

$$\psi_0 = A\Phi_G, \quad \Phi_0 = \prod_G \Phi_G .\qquad(2)$$

The operator A antisymmetrizes Φ_0 with respect to the interchange of electrons belonging to different ions. Using the standard set for numbering of electrons, the Hamiltonian of the solid is given by

$$H = H_0 + V, \quad V = \frac{1}{2}\sum_{GG'}{}' V_{GG'}\qquad(3)$$

where H_0 is the Hamiltonian of the isolated ions with electrons distributed according to the standard set, and $V_{GG'}$ represents interaction between the electrons and nucleus of the G ion with those of the G' ion. In the above V is that part of the total potential which results from interaction between ions and is small compared to the energy of the isolated ions. The energy of the solid is given by

$$E = \frac{\int \widetilde{\psi}_0 H \Phi_0 d\tau}{\int \widetilde{\psi}_0 \Phi_0 d\tau} .\qquad(4)$$

In Eq. (4) ϕ_G corresponds to an isolated ion and no effect of perturbation due to other ions has been considered.

In order to consider the effect of perturbation we introduce the following modified wave function

$$\Phi_0' = \Phi_0 + \sum_G C_G \Phi(G, v)$$

$$+ \sum_{GG'}' C_{GG'} \Phi(Gv, G'v') , \qquad (5a)$$

where the excited states are indicated by the symbol v, e.g., when only the G ion is excited

$$\Phi(G, v) = \Phi_1 \Phi_2 \cdots \Phi_{Gv} . \qquad (5b)$$

To bring out only the essential point we make some simplifying assumptions. In the above, $\Phi(G, v)$ and $\Phi(Gv, G'v')$ are the excited states of the crystal in which only the G ion and only G and G' ions are excited, respectively. Since we are interested in the dipolar deformation of the ions, the individual ion excited states are considered to be p states only. In absence of any external field which is not necessary for our problem we can take the p functions to be real. Further the assumption of the single excited state for each ion leads to the well-known assumption of the energy denominator, the Unsöld approximation. The electron-electron interaction in $V_{GG'}$ will lead to the double excitation envisaged in the last term of Eq. (5a). More than double excitation is disallowed in the present approximation.

The coefficients C_G and $C_{GG'}$ are given by the following expressions:

$$C_G = -\frac{\left\langle 00 \left| \sum_{G'} V_{GG'} \right| Gv, 0 \right\rangle}{E_G} \qquad (6)$$

and

$$C_{GG'} = -\frac{\left\langle 00 \left| \sum_{G'} V_{GG'} \right| Gv, G'v' \right\rangle}{E_G + E_{G'}} . \qquad (7)$$

The coefficient C_G is expressible in terms of the dipole moment developed in the G ion and we keep its value arbitrary. The wave function (5a) implies an electronic dipole moment of the G ion given by

$$\vec{m}_G = -2eC_G \left\langle \Phi_G \left| \sum_i (\vec{r}_i - \vec{R}_G) \right| \Phi_{Gv} \right\rangle , \qquad (8)$$

where Φ_{Gv} is for the G ion in its excited state. Many workers[10,11] have assumed $\vec{m}_G$ to represent the total electronic dipole moment of the G ion, but it actually represents that part of the dipole moment which arises due to perturbation of the wave function. There is another part to it which is contributed by the overlap between the unperturbed wave functions. We demonstrate it by introducing the total dipole moment operator for the crystal,

$$\vec{M} = -\sum e \vec{r}_i + \sum Z_G \vec{R}_G , \qquad (9)$$

where i runs over all electrons and G over all nuclei. The expectation value of M can now be written as

$$\langle \vec{M} \rangle = \frac{\langle \psi_0 | \vec{M} | \Phi_0' \rangle}{\langle \psi_0 | \Phi_0' \rangle} , \qquad (10)$$

where M operates on Φ_0'. We can use the standard set for numbering the electrons in the operation M and can write

$$\vec{M} = -e \sum_{i,G} (\vec{r}_i - \vec{R}_G) + \sum \epsilon_G \vec{R}_G$$

$$= \vec{M}_e + \vec{M}_i . \qquad (11)$$

The second part is the ionic moment with respect to the origin chosen arbitrarily and the first part is the electronic dipole moment operator. Now the mean value in Eq. (10) separates out into two parts, an ionic and an electronic one. For the electronic part $\langle \vec{M}_e \rangle$ we get, retaining terms up to the second-order exchange (S^2, V^2)

$$\langle \vec{M}_e \rangle = \langle \Phi_0 | \vec{M}_e (A - 1) | \Phi_0 \rangle + 2 \sum_G C_G \langle \Phi_0 | \vec{M}_e | \Phi_{Gv} \rangle$$

$$+ 2 \sum_G [C_G \langle \Phi_0 | \vec{M}_e (A - 1) | \Phi_{Gv} \rangle - 2C_G \langle \Phi_0 | \vec{M}_e | \Phi_{Gv} \rangle (A - 1)_{00}^2] . \qquad (12)$$

The above expression for $\langle \vec{M}_e \rangle$ shows that there are three distinct contributions to the electronic di-pole moment. The first term denotes the deformation dipole moment, the second term gives the di-

pole moment due to perturbation of the wave function, and the third term, which gives the second-order exchange dipole moment, is due to both overlap and perturbation. Neglecting the third term we write the total dipole moment as

$$\langle \vec{M}_e \rangle = \sum_G \vec{\mu}_G^d + \sum_G \vec{m}_G = \sum_G \vec{\mu}_G \qquad (13)$$

where the deformation dipole on G due to overlap of its nearest neighbors (NN) is given by

$$\vec{\mu}_G^d = -2e \sum_{\substack{G' \\ (\text{NN of } G)}} \sum_{i,i'} S_{gg'} \int \Phi_{Gi}^*$$

$$\times \Phi_{G'i'}(\vec{r} - \vec{r}_G) d\tau , \qquad (14)$$

where $g = G, i$ and $\vec{m}_G$ is given by Eq. (8). Hence we find that the resultant dipole moment $\vec{\mu}_G$ consists of two parts, one $\vec{\mu}_G^d$ arising out of overlap and another $\vec{m}_G$ due to perturbation of the wave function. It is to be emphasized—a point overlooked by most authors[7,10,11]—that the first term of Eq. (12) will be present even in a rigid-ion model of the ionic solid.

With the above analysis we next write down the energy expression of the solid and discuss the terms of different order. We make a multipole expansion of V in Eq. (3)

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

$$= \frac{1}{2} \sum \left[-\frac{Z_G e^2}{|\vec{R}_a - \vec{r}_{g'}|} - \frac{Z_{G'} e^2}{|\vec{R}_{G'} - r_g|} + \frac{e^2}{|\vec{r}_g - \vec{r}_{g'}|} \right]$$

$$(15)$$

or

$$V = \frac{1}{2} \sum_{GG'}' (m_G m_{G'} + m_G d_{g'} + m_{G'} d_g + d_G d_{G'}) .$$

$$(15b)$$

The monopole-monopole term depends on the nuclear coordinates only and is not an operator. Hence the operation V is of the same order as the operator. We write down the terms in the energy expression as follows.

(a) First order in V and zero order in S^2:

$$E_{10} = \frac{1}{2} \sum_{GG'}' \frac{e_G e_{G'}}{R_{GG'}} + \frac{1}{2} \sum_{GG'}' E_{\text{Co}}(GG') . \qquad (16)$$

The first term is the monopole-monopole interaction between the ions. The second term is the

purely Coulomb overlap energy and vanishes when the charge distribution between ions does not overlap.

(b) First order in V and first order in S^2:

$$E_{11} = S^2 V_{00} - V_{00}^{ex}$$

$$= \frac{1}{2} \sum_{GG'}' \phi(GG') + \sum_G \mu_G^d E_G^m + \cdots \qquad (17a)$$

where the ellipses represent three-body terms and E_G^m is the monopole field at the G ion due to all other ions, where

$$V_{00} = \langle \tilde{\Phi}_0 | V | \Phi_0 \rangle ,$$

$$V_{00}^{ex} = \langle \tilde{\Phi}_0 | V(A - 1) | \Phi_0 \rangle , \qquad (17b)$$

and

$$S^2 = 1 - \int \tilde{\psi}_0 \Phi_0 d\tau ,$$

where $\phi(GG')$ is the two-body overlap energy between the ions G and G'. Usually the Coulomb overlap energy in Eq. (16) is merged with this energy and the total overlap interaction is expressed by the Born-Mayer potential. This is, in fact, the dominant term in the first-order exchange interaction. If we are confined to the S^2 approximation, many-body terms other than three body will vanish. The expression has been discussed in detail by Paul et al.[9] who showed that the three-body terms are the Lundqvist term.[12] A model consisting of terms up to this order only may be termed a rigid-ion model in the sense that all the energy terms arise due to unperturbed wave functions.

(c) Second order in V and zero order in S^2:
This is the pure second-order perturbation term.

$$E_{20} = 2 \sum_v C_v V_{0v} - \sum_v' E_{0v} C_v^2 , \qquad (18a)$$

where

$$V_{0v} = \langle 0 | V | v \rangle , \qquad (18b)$$

where C_v may be either C_G or $C_{GG'}$. It is to be noted that C_v themselves are first order in V and hence both the terms in Eq. (16) are of the order of V^2. Using the multipole of the expansion of V in (15b) and expanding the sums in terms of C_G and $C_{GG'}$ we get after some simplifications

$$E_{20} = -\sum \vec{m}_G \cdot \vec{E}_G + \sum_G \frac{\vec{m}_G^2}{2\alpha_G} - \frac{1}{2} \sum_{GG'}' \frac{A_{GG'}}{R_{GG'}^G} ,$$

$$(18c)$$

where α_G is the polarizability of the G ion and

$A_{GG'}$ is the van der Waals coefficient. The higher-order van der Waals terms are not included in this approximation. The second term is the self-energy term which involves only $\vec{m}_G$ and not the total dipole moment μ_G in Eq. (13).

If we retain terms up to order (2,0) the resulting expression almost corresponds to the phenomenological deformation dipole model.[4] One has to add for consistency the van der Waals and the Lundqvist three-body term.

(d) Second order in V and first order in S^2:

$$E_{21} = 2\sum_{v}' C_v(V_{0v}^{ex} - V_{00}S_{0v}^2)$$
$$-S_{00}^2\left[2\sum_{v}' C_vV_{0v} - \sum_{v}' C_v^2V_{00}\right]$$
$$-\sum_{v\mu}' C_vC_\mu E_{0\mu}S_{\mu v}^2 \tag{19a}$$

with

$$S_{00}^2 = \langle 0|(A-1)|0\rangle, \quad S_{0v}^2 = \langle 0|(A-1)|v\rangle,$$
$$S_{\mu v}^2 = \langle \mu|(A-1)|v\rangle,$$

and $\tag{19b}$

$$V_{0v} = \langle 0|V|v\rangle, \quad V_{0v}^{ex} = \langle v|V(A-1)|0\rangle,$$

where C_v is C_G or $C_{GG'}$. In this order terms involve both overlap and exchange with the perturbed wave functions and all of them imply short-range interactions. We shall presently discuss the precise approximations under which the most important term in Eq. (19a) will lead to the short-range polarization mechanism envisaged in the shell model. Before that we consider the second term. The portion within the parentheses is identical with Eq. (18a) and hence the second term is very clearly interpreted as the modification of the second-order energy (18a) due to overlap. This includes, for example, the change in the van der Waals energy when the charge clouds of two ions overlap. These effects are too difficult to estimate. Until now no attempt has been made, to our knowledge, to tackle them and no phenomenological model tries to include these terms. The most significant is, however, the first term. We consider only those terms for which C_v is C_G. One may try to replace C_G in terms of the dipole moment through Eq. (8), but difficulty arises since the excited states here are the p states which are three-fold degenerate. The three p states in Φ_{Gv} constitutes a vector and hence C_G is also a vector and a dot product between C_G and Φ_{Gv} is implied in Eq. (8). However, we can get an idea of this term

under some simplifying assumptions. Let us consider two ions G and G' separated by a distance $R_{GG'}$. We take the Z axis along $R_{GG'}$ and assume that the dipole moments $\vec{m}_G$ and $\vec{m}_{G'}$ are also along this direction. In this case C_G reduces to a single component and we may write the first term in Eq. (19a)

$$E_{21}^I = \sum_{v}' c_v(V_{0v}^{ex} - V_{00}S_{0v}^2)$$
$$= -\left[\frac{\vec{m}_G\phi_{v0}(GG')}{2en_G\zeta_G} + \frac{\vec{m}_{G'}\phi_{0v}(GG')}{2en_{G'}\zeta_{G'}}\right], \tag{19c}$$

where

$$\zeta_G = \left\langle \Phi_G \left| \sum_i (r_i - R_G)_z \right| \Phi_{G,v} \right\rangle \tag{19d}$$

and $\phi_{v0}(GG')$ is the overlap interaction between G and G' ions when an electron in the G ion is in an excited state. If we further make this assumption that the overlap does not substantially alter when only one of the electrons in the ions concerned is excited, we can set $\phi_{v0}(GG') = \phi_{0v}(GG') \simeq \phi(GG')$. This is quite justified since the overlap interaction involves all the electrons belonging to both the ions and as such the perturbation of a single electron will not significantly alter the total interaction energy. With this assumption E_{21}^I reduces to

$$E_{21}^I = -\left[\frac{\vec{m}_G}{\eta_G} + \frac{\vec{m}_{G'}}{\eta_{G'}}\right]\phi(GG'), \tag{19e}$$

where

$$\eta_G = 2en_G\zeta_G$$

which is identical with the phenomenological shell-model expression for the change in overlap interaction between two ions when they have dipole moment. This is given by (see Sarkar and Sengupta[13])

$$-\left[\frac{\vec{m}_G}{Y_G\rho} + \frac{\vec{m}_{G'}}{Y_{G'}\rho}\right]\phi(GG'), \tag{20}$$

where $\phi(GG') = b\exp(-R_{GG'}/\rho)$ is the overlap interaction and $-Y_G$ is the shell change of the G ion. The similarity between the expression (19e) and (20) is quite striking and in fact Eq. (19e) furnishes a direct quantum-mechanical justification of (20) which is the pivotal assumption on which the shell model is based. As the actual quantum-mechanical evaluation of the entire second-order exchange interaction is extremely difficult we simplify it in view of the above discussion by writing

the major effect of the second-order exchange term by

$$E_{21} \simeq \phi(\vec{R}_{GG'}, \vec{m}_G, \vec{m}_{G'})$$

$$= \phi\left(\left| \vec{R}_{GG'} - \frac{m_G}{Y_G} + \frac{m_{G'}}{Y_{G'}} \right|\right) - \phi(R_{GG'}) \ .$$

(21)

The last term in Eq. (19a) for which C_v is $C_{GG'}$ is also neglected. In this approximation the entire effect of the second-order exchange interaction is to alter the short-range overlap interaction obtained from the first-order exchange due to the formation of the dipole moments in the ions.

We restrict our analysis up to this order. It is expected that the terms beyond this may not be important. However, no investigation has so far been attempted to prove the importance or unimportance of them. If these are to be considered one has to extend the quantum-mechanical calculation to S^4 order.

III. MODEL

In this section we utilize the above analysis to construct the model we propose for the investigation of the dielectric properties. The total energy expression for an ionic solid with arbitrary position of ions is given by (see also Refs. 11 and 13)

$$W = \frac{1}{2} \sum_{i,j}{}' \frac{Z_i Z_j}{r_{ij}} - \sum_i \vec{\mu}_i (\vec{E}_i^m + \frac{1}{2} \vec{E}_i^\mu) + \sum_i \frac{\vec{m}_i^2}{2\alpha_i}$$

$$+ \frac{1}{2} \sum_{i,j}{}' - \frac{C_{ij}}{r_{ij}^6} + \frac{1}{2} \sum_{i,j}{}' \phi(r_{ij})$$

$$+ \frac{1}{2} \sum_{i,j}{}' \phi(r_{ij}, \vec{m}_i, \vec{m}_j) \qquad (22a)$$

with

$$\vec{\mu}_i = \vec{\mu}_i^d + \vec{m}_i \ ,$$

where $\vec{\mu}_i^d$ and $\vec{m}_i$ are the deformation dipole due to first-order exchange charges and the dipole moment due to the perturbation of the wave function, respectively. $\vec{E}_i^m$ and $\vec{E}_i^\mu$ indicate the monopole and dipole field, respectively. Since we are interested in the polarization effect only we also neglect the three-body interaction term, i.e., the Lundqvist term in the first-order exchange. The first term in Eq. (22a) corresponds directly to Eq. (16). The second term corresponds to Eqs. (17a) and (18c). The third term is the self-energy term and is the

same as the second term in (18c). It is to be noted that since self-energy involves the perturbation of the wave functions, $\vec{m}_i$ and not the total $\vec{\mu}_i$ represents this. The first three terms represent the pure electrical contributions. The fourth one is the van der Waals interaction and corresponds to Eq. (18c). The fifth one is the two-body overlap interaction term in Eq. (17a), and the last term represents the change in overlap interaction due to the perturbation of the wave functions and corresponds to Eq. (21).

Before we proceed further with the calculation it will be instructive to discuss the polarization mechanisms of the deformation dipole model and the shell model in light of the above analysis and energy expression. We find[14] from the above analysis that the total dipole moment in an ion is caused by two factors—one is due to redistribution of exchange charges which arise when the overlap between the two ions take place with unperturbed wave functions. This is, in fact, the quantum-mechanical origin of the short-range polarizability first suggested by Szigeti[15] and Hardy[4] and Karo later developed this idea in their deformation dipole model. The corresponding dipole moment is expressed by $\vec{\mu}^d$ in Eq. (14). Consequently there is no self-energy term corresponding to this deformation dipole. Again, expression (14) shows that it is essentially a short-range effect and it vanishes if overlap is absent. Further it is to be noted that this dipole polarizability does not contribute anything to the high-frequency dielectric constant of the solid which we shall discuss later. The second effect is due to perturbation of the wave function caused by the Coulomb field of the other ions. This gives rise to the usual long-range electric field polarizability given by $\vec{m}_G$ [see Eqs. (8) and (18a)]. Apart from this the perturbation may also be due to a short-range effect due to second-order exchange envisaged in Eq. (21). This is also connected with the overlap interaction which involves perturbation of the wave function. And in fact this is the origin of the short-range polarization mechanism in the shell model. If we exclude $\vec{\mu}_i^d$ in W, the energy expression becomes identical with that of the shell model. And if we exclude the last term in Eq. (22a), it reduces to the energy expression of the deformation dipole model. To conclude we state that the shell model and the deformation dipole model describe two entirely different short-range polarization mechanisms which are complementary to each other and unlike the deformation dipole model the short-range polarization mechanism in the shell model affects both the high-

frequency and the low-frequency dielectric constants. Hence any complete theory must include both of them. In literature there are several comparisons[10,16] of these two models and nowhere has their quantum-mechanical origin been so clearly traced.

Next, in order to develop the dielectric equations we assume the following forms of the overlap interaction in Eq. (22a):

$$\phi(r_{ij}) = b \exp(-r_{ij}/\rho) , \qquad (22b)$$

$$\phi(\vec{r}_{ij}\vec{m}_i) = b \exp -\frac{1}{\rho} \left| \vec{r}_{ij} - \frac{\vec{m}_i}{m_{0i}} \right| -\phi(r_{ij}) , \qquad (22c)$$

$$\vec{\mu}_i^d = \sum_j D(ji)U_j = -\sum m_i'(r_{ij})\frac{\vec{r}_{ij}}{r_{ij}} ,$$

and   (22d)

$$m_i'(r_{ij}) = C \exp(-r_{ij}/\rho') ,$$

where b and ρ are the usual short-range interaction parameters and m_{0i} is a parameter having the dimension of charge. It has been shown in Refs. 13 and 16 that if we substitute $\alpha_i = Y_i^2/K_i$ and $m_{0i} = Y_i$ the usual shell-model expressions are obtained (Y and K being the shell charge and core-shell spring constant). In writing Eq. (22c) we have assumed that the dipole moment is associated only with the negative ion which, as is well known, corresponds to the negative ion polarizable shell model. A comment appears to be in order regarding the specific form we have chosen for $\phi(r_{ij},\vec{m}_i)$. We have been guided by two considerations. Starting from the Clementi wave functions, Basu and Sengupta[18] have directly calculated numerically the change in the overlap function when the negative ion is perturbed by a dipolar distortion and have shown its variation with the distance of separation between the two ions. It has been found that the change in overlap function in the presence of a dipole moment may be quite adequately represented by the form given in (22c). On the pure empirical level this form as already demonstrated (see Ref. 13) is identical with that of a shell model. The form for μ_i^d has been assumed after Hardy[4] and Karo.

Equation (22a) represents our complete model for the present calculation where all the terms have *a priori* quantum-mechanical justification. This equation together with the so-called adiabatic condition

$$\frac{\partial W}{\partial \vec{m}_i} = 0 \qquad (23)$$

determines, in fact, all the lattice mechanical properties.

Now expanding $\vec{r}_{ij}$ in Eq. (22a) about the equilibrium position the dynamical equations can be written in the usual six-vector notation as follows (see Sarkar and Sengupta[13])

$$[(Z+D)C(Z+D^T)+R]\vec{U}$$
$$+[(Z+D)C-R\mu^{-1}]\vec{M} = m\omega^2\vec{U} , \qquad (24)$$

$$[-C(Z+D^T)-\mu^{-1}R]\vec{U}$$
$$+(C+\alpha^{-1}+\mu^{-1}R\mu^{-1})\vec{M} = 0 ,$$

where $\vec{U} = (\vec{U}_1,\vec{U}_2)$ and $\vec{M} = (\vec{M}_1,\vec{M}_2)$ are the displacement and the dipole fluctuation vectors, $\vec{Z}$, $\vec{\alpha}$, and $\vec{m}$ are the 6×6 matrices for the ionic charge, the ionic polarizability, and the ionic mass, respectively. $\vec{R}$, $\vec{C}$, and $\vec{\mu}$ are the overlap interaction, the Coulomb interaction, and the short-range polarizability matrices, respectively. D represents the matrix corresponding to the deformation dipole.

The above equation in the limit of the $\vec{q} = 0$ condition will yield the dielectric equations. The force equations are given by

$$m_1\ddot{U}_1 = Z_1 E_{\text{eff}} - D(11)E_{\text{eff}}$$
$$-R_0(U_1-U_2) - \frac{R_0}{m_0}\mu_2 , \qquad (25)$$

$$m_2\ddot{U}_2 = Z_2 E_{\text{eff}} - D_0 E_{\text{eff}}$$
$$-R_0(U_2-U_1) + \frac{R_0}{m_0}\mu_2 ,$$

and the polarization per unit volume

$$P = Z_1 U_1 + Z_2 U_2 + \mu_2^d + \mu_2 , \qquad (26)$$

and the adiabatic equation is

$$0 = -m_0 E_{\text{eff}} + \left[\frac{m_0}{\alpha_2} + \frac{R_0}{m_0}\right]\mu_2 - R_0(U_2-U_1) \qquad (27a)$$

or   (27b)

$$\mu_2 = a_2 E_{\text{eff}} + b_2 U ,$$

where

$$a_2 = 1 \Big/ \left[\frac{1}{\alpha_2} + \frac{R_0}{m_0^2} \right]$$

and

$$b_2 = (-1) \frac{R_0 a_2}{m_0} .$$

Hence

$$P = [Z_1' - D(22)] U + a_2 E_{\text{eff}} , \qquad (26')$$

where

$$Z_1' = Z_1 - \frac{R_0 a_2}{m_0} = -Z_2 .$$

Using the above expression for μ_2 in Eq. (25) we can write the force equation as

$$m_i \ddot{\vec{U}}_i = Z_i \vec{E}_{\text{eff}} + C_i \vec{U} , \qquad (28)$$

where

$$C_1 = R_0 + \frac{R_0 b_2}{m_0} = -C_2 .$$

Next using $\underline{W} = \bar{m} \vec{U}$ ($\bar{m}$ is the reduced mass) and the Lorentz expression for $\underline{E}_{\text{eff}}$, we can write the Huang relations,[18]

$$\ddot{\vec{W}} = b_{11} \vec{W} + b_{12} \vec{E} ,$$
$$\qquad (29)$$
$$\vec{P} = b_{12} \vec{W} + b_{22} \vec{E} ,$$

where

$$b_{11} = -\frac{1}{\bar{m}} \left[C_1 - \frac{\frac{4\pi}{3v} (Z_1'')^2}{1 - \frac{4\pi}{3v} a_2} \right] , \qquad (30a)$$

$$b_{22} = \frac{a_2}{v} \frac{1}{1 - \frac{4\pi}{3v} a_2} , \qquad (30b)$$

$$b_{12} = \frac{Z_1''}{(\bar{m}v)^{1/2}} \frac{1}{1 - \frac{4\pi}{3v} a_2} , \qquad (30c)$$

with

$$C_1 = R_0 - \frac{R_0^2 a_2}{m_0^2} ,$$

$$Z_1'' = Z_1' - D_0 .$$

The three macroscopic dielectric properties, namely the high- and low-frequency dielectric constants

ϵ_∞, ϵ_0 and the restrahlen frequency ω_0 are related to the b's by the following equations:

$$\epsilon_\infty = 1 + 4\pi b_{22} , \qquad (31a)$$

$$\omega_{70}^2 = -b_{11} , \qquad (31b)$$

and

$$\epsilon_0 = \epsilon_\infty - \frac{4\pi b_{12}^2}{b_{11}} . \qquad (31c)$$

An inspection of Eqs. (30) and (31) immediately shows that there is a contribution to the high-frequency dielectric constant only from the dipole moment generated out of the perturbation of the wave function. This is evident since the term a_2 consists only of two parts:

$$\frac{1}{a_2} = \frac{1}{\alpha_2} + \frac{R_0}{m_0^2} .$$

The first one is the pure second-order perturbation effect and the second one is the second-order exchange effect. No contribution from the first-order exchange effect occurs to ϵ_∞. Unlike the case of ϵ_∞, there are contributions both from the first-order exchange and the second-order exchange interaction to ϵ_0. The factor Z_1'' consists of three parts:

$$Z_1'' = Z_1 - D_0 - \frac{R_0 a_2}{m_0} .$$

The first term is the ionic charge. The second and third terms arise out of the first-order exchange and the second-order exchange interaction, respectively. In the shell-model dielectric theory the term D_0 does not occur. Hence we presume that this additional effect may be important in describing the pressure derivative of the static dielectric constant. This is more so in view of the fact that it has strong dependence on the interionic separation.[19] In the next section we consider an application of the above model to discuss the pressure derivative of the static dielectric constants.

IV. CALCULATION OF THE PRESSURE DERIVATIVE OF ϵ_0

In the present model we have altogether six parameters, namely b and ρ, the short-range overlap parameters, m_0 and α_2, the polarization parameters connected with the perturbed wave function (these correspond to Y and K of the shell model), and C and ρ', the first-order exchange parameters.

TABLE I. Calculation of the pressure derivative of the low-frequency dielectric constants $(d\epsilon_0/dp$ in $10^{-12})$. All entries are to be taken with a negative sign.

	Present calculation		
	Without first-order	With first-order	
Crystal	exchange	exchange	Expt.
KCl	41.96	45.0	49.85[b]
KBr	52.32	54.53	57.94[b]
KI	62.29	64.70	70.01[a]
NaCl	67.45	68.81	57.44[b]
NaBr	99.02	99.70	79.78[b]
RbCl	40.25	47.35	49.98[a]
RbBr	32.94	58.74	57.74[a]
RbI	82.58	72.76	66.06[a]

[a]Reference 20.
[b]Reference 21.

In a complete calculation we must organize a fit of the different lattice mechanical properties of a crystal in terms of the above parameters and with the values of parameters thus determined we should calculate the pressure derivative. But since in this preliminary application we are not interested in an exact fit, rather we want to make a rough estimate of the additional effect we have obtained for the static dielectric constant, we use the values of the parameters used earlier for the calculation of the pressure derivative of the high-frequency dielectric constants for the same crystals. Of the two additional parameters, namely C and ρ', C is determined from the experimental value of the restrahlen frequency using the expression (31b). The other constant ρ' is fixed at 1.90 Å from the experimental value of the pressure derivative of a crystal taken arbitrarily. We presume that the value of ρ' like the overlap parameter ρ will remain more or less the same for all crystals. We have had recourse to this procedure because in this method two things may be clearly demonstrated. Firstly, with the present set of parameters the previous calculation[1] for the pressure derivative of the high-frequency dielectric constants remain unaltered. Secondly, it will give a rough idea about the order of magnitude of the effect of first-order exchange interaction. The results of our present calculation with and without this effect are shown in Table I together with observation.

V. DISCUSSION

The present investigation indicates that the two types of polarization mechanisms obtained from a microscopic analysis of the energy expression are important in describing the low-frequency dielectric constant and its pressure derivative. It is of further importance to note in this connection that the shell model of the deformation dipole model is more or less adequate in describing the dielectric constants but in order to discuss the pressure derivatives a combination of both the short-range polarization mechanisms is necessary. In particular this is required for the pressure derivative of the static dielectric constants. This is understandable in view of the fact that the finer details of the polarization effect will be magnified in these properties.

An examination of the results of the present calculation shows that the inclusion of the first-order exchange effect improves the agreement in the right direction in the majority of cases. Our choice of the crystals has been motivated by our previous calculation for which the parameters are available. For the two crystals NaCl and NaBr, there is no significant improvement. This is presumably because the assumption of the same value of ρ' for all crystals is too stringent. It is preferable to fix the value of ρ' for each crystal separately. However, this preliminary calculation definitely indicates the significance of this interaction. In addition, the present results together with our previous calculations for the pressure derivative of the high-frequency dielectric constants show that it is possible to describe both the high-frequency and low-frequency dielectric behavior of the alkali halide crystals in the framework of a single model and with the same set of parameters. Before we conclude it is to be noted that we have emphasized in the present work the importance of

the two polarization effects only in the dielectric properties of the crystals. But it is evident from the dynamical equations that the first-order exchange dipole will also affect the phonon frequen-

cies: In a future communication we plan to investigate the relative importance of these two effects on the dispersion of phonons.

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