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Deformation dipole model and lattice dynamics of zinc-blende-structure compounds*

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The deformation-dipole-model (DDM) formalism is derived for a crystal of arbitrary symmetry and applied to the zinc-blende structure. In its present form, the model is more general than the one proposed by Karo and Hardy, the principal difference consisting in introducing interactions called nonlocal electric polarizabilities, analogous to the shell-shell interactions of the shell model. Both approaches are compared and it is shown that in ionic crystals the present version of the DDM provides the same description of core motion as the shell model. Parameters of one model are then expressed in terms of the other model, for ionic structures; the case of covalent crystals is also briefly discussed. A simplified form of the DDM was used in numerical calculations for 15 crystals with T_d^4 symmetry. Model parameters fitted to elastic, piezoelectric, optical and, for eight compounds, also to neutron-diffraction measurements gave a good description of phonon frequencies. Some of the parameters appeared to be smoothly varying functions of the interatomic distance or ionicity.

I. INTRODUCTION

During the last decade the development of neutron spectroscopy has stimulated a rapid development of lattice dynamics of semiconducting compounds. Various models have been proposed to describe the long-range part of interatomic forces, which is due to electrostatic interactions in the system of cores and loosely or tightly bound electrons. Besides the rigid-ion model it was the shell model that was most frequently used in connection with neutron measurements, and its 14-parameter version was successively applied by different authors to several compounds having the zinc-blende structure. It was our aim to examine the extent to which it is possible to apply the deformation-dipole model (DDM) to this group of crystals.[1] So far this model has been systematically exploited only for the description of strongly ionic crystals.[2,3] We have used this model for a simultaneous study of the lattice dynamics of 15 compounds having T_d^4 symmetry. This set of tetrahedrally coordinated compounds is convenient for our investigation since it provides examples of bonding ranging from highly ionic to highly covalent.

The DDM proposed in this paper is a generalization of the model presented by Karo and Hardy.[2,3] The latter model, which was applied to some crystals of rock-salt structure, may be considered as a particular version of our more general DDM. In this article we concentrate our attention mainly upon the conceptual and formal aspects of DDM and we mention briefly only some of the results of the actual numerical calculations, which are more thoroughly discussed elsewhere.[4,5]

Like other models, the DDM is based on the adiabatic, harmonic, and linear-dipole approximations, and situates all the electric dipoles at lattice sites only. In this respect it can be classed in the same category as, e.g., the shell model[6-8] or the model of Mashkevitch and Tolpygo.[9,10] We derive in Sec. II the basic equations of the DDM starting from the macroscopic description of crystal. Unlike the preceding works,[2,3] we write the relation between the electric polarization and the local electric field in a general form; for this purpose we have to introduce the nonlocal electric polarizabilities which have not been considered explicitly so far. We shall show that the equations of motion which govern the DDM are analogous to the corresponding equations of the shell model. The formalism, written in Sec. II for a crystal of arbitrary symmetry, is then applied in Sec. III to the zinc-blende structure, and the form of the matrices of "polarizabilities," "deformabilities," and short-range coupling parameters is written down for this structure.

In Sec. IV the DDM is compared to the shell model. It is found that in ionic crystals a formal equivalence may be established between both models and relations are derived between the parameters of the (general) DDM and those of the shell model. This equivalence concerns the description of core motion: the electric dipoles appearing on lattice sites may still be predicted differently by both models. In covalent crystals the expressions relating the parameters of the two models hold only approximately and a correspondence between them cannot be established in a straightforward manner. Various approximations imposed to one model are then discussed in terms of the other one. In particular, it is shown that the neglect of nonlocal polarizabilities (Karo-Hardy version of DDM) is equivalent to the neglect of the shell-shell interactions in the shell model.

Some results of numerical calculations with the DDM are then given in Sec. V. After certain simplifications the model was applied to 15 compounds with zinc-blende structure; for eight of them (ZnS, ZnSe, GaP, GaAs, InSb, SiC, CuCl, and CuI) a complete fit of the 15-parameter version could be obtained. Dispersion curves in reasonable agreement with neutron measurements were obtained for these materials. Particular care was taken in the development of an appropriate method for the determination of the model parameters: A succession of physically motivated simplifications was used in this procedure. Certain trends appeared when some of the parameters were plotted against ionicity or interatomic distance.

II. DEFORMATION-DIPOLE MODEL

When the forces between the constituents of a crystal are supposed to be partly or completely of electrostatic origin, we must consider its (total) dipole moment $\bar{M}_\alpha(\ldots \vec{r}(l\kappa)\ldots)$, $\alpha = 1, 2, 3$. The latter can be developed with respect to the displacements $u_\alpha(l\kappa)$ in the same way as the potential energy $\Phi(\ldots \vec{r}(l\kappa)\ldots)$ of the crystal,[11]

$$\bar{M}_\alpha = \bar{M}^0_\alpha + \sum_{l\kappa\beta} \bar{M}_{\alpha\beta}(l\kappa) u_\beta(l\kappa) + \cdots , \tag{1}$$

higher than linear terms being neglected. Here $\bar{M}^0_\alpha$ are the components of the permanent dipole moment and the coefficients

$$\bar{M}_{\alpha\beta} \equiv \left. \frac{\partial \bar{M}_\alpha(\ldots \vec{r}(l\kappa)\ldots)}{\partial u_\beta(l\kappa)} \right|_0 \tag{2}$$

are evaluated at equilibrium. They have to satisfy certain conditions, analogous to those obeyed by coupling parameters $\Phi_{\alpha\beta}$. In particular, as the crystal is electrically neutral, a rigid-body translation

$$u_\alpha(l\kappa) = v_\alpha \tag{3}$$

does not alter its total dipole moment; therefore

$$\sum_{l\kappa} \bar{M}_{\alpha\beta}(l\kappa) = 0. \tag{4}$$

If the symmetry operation $\{\underline{S} \,|\, \vec{v}(S) + \vec{x}(m)\}$ transforms the site $(l\kappa)$ into (LK),

$$\{\underline{S} \,|\, \vec{v}(S) + \vec{x}(m)\} \vec{x}(l\kappa) = \underline{S}\vec{x}(l\kappa) + \vec{v}(S) + \vec{x}(m) \equiv \vec{x}(LK) , \tag{5}$$

then the symmetry of the crystal imposes on $\bar{M}_{\alpha\beta}(l\kappa)$ the transformation law[12]

$$\bar{M}_{\alpha\beta}(LK) = \sum_{\mu\nu} S_{\alpha\mu} S_{\beta\nu} \bar{M}_{\mu\nu}(l\kappa) , \tag{6}$$

and we find immediately that $\bar{M}_{\alpha\beta}(l\kappa)$ is independent of l. To improve our understanding of the physical meaning of parameters we decompose $\bar{M}_{\alpha\beta}(l\kappa)$ into contributions coming from individual lattice sites,

$$\bar{M}_{\alpha\beta}(l\kappa) \equiv \sum_{l'\kappa'} M_{\alpha\beta}(l'\kappa'; l\kappa) , \tag{7}$$

and we choose every parameter $M_{\alpha\beta}(l\kappa; l'\kappa')$ so as to represent the α component of the dipole moment which is induced on the site $(l\kappa)$ when the atom $(l'\kappa')$ is displaced a unit distance in the β direction:

$$p_\alpha(l\kappa) = \sum_{l'\kappa'} M_{\alpha\beta}(l\kappa; l'\kappa') u_\beta(l'\kappa') . \tag{8}$$

It should be noted that the decomposition (7) is somewhat arbitrary, namely, to the same extent as the notion of a dipole situated on a given lattice site: Whereas $\bar{M}_{\alpha\beta}(l\kappa)$ in (1) was still a measurable quantity in some *Gedankenexperiment*, we need a *model* to realize a decomposition (7) which would satisfy (8). We also may say that (7) together with (8) *is* a model.

The choice of model [i.e., the definition of the coefficients $M_{\alpha\beta}(l\kappa; l'\kappa')$] may further be facilitated if we write (8) as a sum of two terms:

$$M_{\alpha\beta}(l\kappa; l'\kappa') \equiv e_{\alpha\beta}(l\kappa)\, \delta_{ll'} \delta_{\kappa\kappa'} + m_{\alpha\beta}(l\kappa; l'\kappa'). \tag{9}$$

The dipole (8) induced on $(l\kappa)$ can now be interpreted as coming from two mechanisms: from the displacements of the charge $e_{\alpha\beta}(l\kappa)$ of the site $(l\kappa)$ and from the deformation of the electronic charge distribution in the crystal

$$p_\alpha(l\kappa) = \sum_\beta e_{\alpha\beta}(l\kappa)\, u_\beta(l\kappa) + \sum_{l'\kappa'\beta} m_{\alpha\beta}(l\kappa; l'\kappa')\, u_\beta(l'\kappa'). \tag{10}$$

In order that the partition (9) may really have the above meaning, a rigid translation (3) of the crystal should not give rise to any deformation producing only the dipoles

$$\sum_\beta e_{\alpha\beta}(l\kappa)\, v_\beta . \tag{11}$$

Therefore we have to require

$$\sum_{l'\kappa'} m_{\alpha\beta}(l\kappa; l'\kappa') = 0, \tag{12}$$

which implies

$$e_{\alpha\beta}(l\kappa) = \sum_{l'\kappa'} M_{\alpha\beta}(l\kappa; l'\kappa'). \tag{13}$$

The splitting (9) of $\underline{M}$ into $\underline{e}$ and $\underline{m}$ thus did not introduce any new redundant parameters. The elements of the matrix $\underline{m}$ are called "mechanical polarizabilities" or "deformabilities."

Conditions (6) and (12) are immediately reformulated as requirements for $\underline{e}$, $\underline{m}$:

$$\sum_{l\kappa} e_{\alpha\beta}(l\kappa) = 0, \tag{14}$$

$$e_{\alpha\beta}(LK) = \sum_{\mu\nu} S_{\alpha\mu}\, S_{\beta\nu}\, e_{\mu\nu}(l\kappa), \tag{15}$$

$$m_{\alpha\beta}(LK; L'K') = \sum_{\mu\nu} S_{\alpha\mu}\, S_{\beta\nu}\, m_{\mu\nu}(l\kappa; l'\kappa'). \tag{16}$$

The last two equations imply that $e_{\alpha\beta}(l\kappa)$ is independent of l and that $m_{\alpha\beta}(l\kappa; l'\kappa')$ depends only on $l' - l$. The condition (14) of charge neutrality of the crystal thus becomes

$$\sum_{\kappa} e_{\alpha\beta}(\kappa) = 0. \tag{17}$$

Finally, we have to account for the response of the electronic charge to the microscopic electric field. This is done by introducing "electronic polarizabilities" $a_{\alpha\beta}(l\kappa; l'\kappa')$ so that the total dipole moment induced on the site $(l\kappa)$ can be written

$$\begin{aligned} p_\alpha(l\kappa) = & \sum_\beta e_{\alpha\beta}(\kappa) u_\beta(l\kappa) \\ & + \sum_{l'\kappa'\beta} m_{\alpha\beta}(l\kappa; l'\kappa') u_\beta(l'\kappa') \\ & + \sum_{l'\kappa'\beta} a_{\alpha\beta}(l\kappa; l'\kappa')\, E^{\mathrm{eff}}_\beta(l'\kappa'). \end{aligned} \tag{18}$$

Here $\vec{E}^{\,\mathrm{eff}}(l\kappa)$ stands for the effective electric field on the site $(l\kappa)$, i.e., the field produced by the dipoles (18) on all the lattice sites except $(l\kappa)$ itself. Allowing for terms $a_{\alpha\beta}(l\kappa; l'\kappa')$, we are taking into account the "polarization" of the site $(l\kappa)$ by the electric field on the site $(l'\kappa')$. The symmetry property

$$a_{\alpha\beta}(LK; L'K') = \sum_{\mu\nu} S_{\alpha\mu}\, S_{\beta\nu}\, a_{\mu\nu}(l\kappa; l'\kappa') \tag{19a}$$

can be derived directly from (18). The nondiagonal blocks of the matrix $\underline{a}$ will be responsible for the wave-vector dependence of the Fourier-transformed matrix $\underline{a}(\vec{k})$ in (28b). The requirement of its Hermiticity[13] imposes

$$a_{\alpha\beta}(l\kappa; l'\kappa') = a_{\beta\alpha}(l'\kappa'; l\kappa) \tag{19b}$$

in addition to (19a). There is in general no reason[14] to consider only the terms with $(l'\kappa') = (l\kappa)$ (called local polarizabilities), and we shall see in Sec. IV that the nonlocal terms may play an important role in covalent crystals.

The force acting on the atom $(l\kappa)$,

$$\begin{aligned} F_\alpha(l\kappa) = & -\sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa; l'\kappa')\, u_\beta(l'\kappa') \\ & + \sum_\beta e_{\alpha\beta}(\kappa)\, E^{\mathrm{eff}}_\beta(l\kappa) \\ & + \sum_{l'\kappa'\beta} m_{\beta\alpha}(l'\kappa'; l\kappa)\, E^{\mathrm{eff}}_\beta(l'\kappa'), \end{aligned} \tag{20}$$

is that acting on the dipole in the electric field (the second and third terms) plus a short-range force representing all the other interactions, not considered so far (the first term). The coefficients $\Phi_{\alpha\beta}(l\kappa; l'\kappa')$ are the usual Born–von Kármán coupling parameters whose transformation law is well known[15]

$$\Phi_{\alpha\beta}(LK; L'K') = \sum_{\mu\nu} S_{\alpha\mu}\, S_{\beta\nu}\, \Phi_{\mu\nu}(l\kappa; l'\kappa'). \tag{21}$$

Equations (18) and (20), which are written for a crystal of arbitrary symmetry, define the deformation-dipole model. If the nonlocal polarizabilities $\underline{a}(l\kappa; l'\kappa')$, $l\kappa \neq l'\kappa'$ are neglected in (18), we obtain that particular version of the DDM which was proposed by Karo and Hardy[2,3] and which was applied to several crystals of rock-salt structure.[3,16–22] At present, there exist no numerical calculations with the DDM in its full generality which would take explicitly into account the nonlocal polarizabilities. Our results, which are briefly summarized in Sec. V, were obtained in an approximation which does not go beyond the frame of the Karo-Hardy model either. The existing shell-model calculations account for nonlocal polarizabilities implicitly, as will be shown in Sec. IV.

III. APPLICATION TO ZINC-BLENDE STRUCTURE

We put the origin on the metallic atom labeled by $\kappa = 1$; the atom of nonmetal $\kappa = 2$ will be situated at the site $(\frac{1}{4}a)$ (1, 1, 1), where a denotes the lattice constant.

The symmetry of the lattice imposes upon the short-range coupling parameters $\Phi_{\alpha\beta}(l\kappa; l'\kappa')$ the form

$$\Phi(\vec{0}, 1; \vec{0}, 2) \equiv \Phi(\mathrm{Zn}; \mathrm{S}) = \begin{bmatrix} A & B & B \\ B & A & B \\ B & B & A \end{bmatrix}, \tag{22a}$$

$$\Phi(\vec{0}, 1; (\tfrac{1}{2}a)(1, 1, 0), 1) \equiv \Phi(\mathrm{Zn}; \mathrm{Zn}) = \begin{bmatrix} C_1 & D_1 & E_1 \\ D_1 & C_1 & E_1 \\ -E_1 & -E_1 & F_1 \end{bmatrix}, \tag{22b}$$

$$\Phi(\vec{0}, 2; (\tfrac{1}{2}a)(1, 1, 0), 2) \equiv \Phi(\mathrm{S}; \mathrm{S}) = \begin{bmatrix} C_2 & D_2 & -E_2 \\ D_2 & C_2 & -E_2 \\ E_2 & E_2 & F_2 \end{bmatrix}. \tag{22c}$$

We remark that the transformation law for the mechanical and electric polarizability tensors $\underline{m}$

and $\underline{a}$, Eqs. (16) and (19), is the same as that for Φ, Eq. (21), except, however, that $m_{\alpha\beta}(l\kappa;l'\kappa') \neq m_{\beta\alpha}(l'\kappa';l\kappa)$. We also note that the diagonal blocks $\underline{a}(l\kappa;l\kappa)$ cannot be derived from the nondiagonal ones by any condition of translational invariance analogous to (12). We may write immediately,[23] by analogy with (22a),

$$\underline{m}(\vec{0},1;\vec{0},2) \equiv \underline{m}(\mathrm{Zn};\mathrm{S}) = \tfrac{1}{3}\begin{bmatrix} -\gamma_1 & -\gamma_3 & -\gamma_3 \\ -\gamma_3 & -\gamma_1 & -\gamma_3 \\ -\gamma_3 & -\gamma_3 & -\gamma_1 \end{bmatrix}, \tag{23a}$$

$$\underline{m}(\vec{0},2;\vec{0},1) \equiv \underline{m}(\mathrm{S};\mathrm{Zn}) = \tfrac{1}{3}\begin{bmatrix} +\gamma_2 & +\gamma_4 & +\gamma_4 \\ +\gamma_4 & +\gamma_2 & +\gamma_4 \\ +\gamma_4 & +\gamma_4 & +\gamma_2 \end{bmatrix}, \tag{23b}$$

the diagonal blocks like $\underline{m}(\vec{0},1;\vec{0},1)$, etc., then being given by (12):

$$m_{\alpha\beta}(\vec{0},1;\vec{0},1) \equiv m_{\alpha\beta}(\mathrm{Zn};\mathrm{Zn}) = \tfrac{4}{3}\gamma_1\,\delta_{\alpha\beta};$$
$$m_{\alpha\beta}(\vec{0},2;\vec{0},2) \equiv m_{\alpha\beta}(S;S) = -\tfrac{4}{3}\gamma_2\,\delta_{\alpha\beta}, \tag{23c}$$

and

$$\underline{a}(\vec{0},1;\vec{0},1) \equiv \underline{a}(\mathrm{Zn};\mathrm{Zn}) = \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_1 \end{bmatrix}, \tag{24a}$$

$$\underline{a}(\vec{0},2;\vec{0},2) \equiv \underline{a}(\mathrm{S};\mathrm{S}) = \begin{bmatrix} \alpha_2 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_2 \end{bmatrix}, \tag{24b}$$

$$\underline{a}(\vec{0},1;\vec{0},2) \equiv \underline{a}(\mathrm{Zn};\mathrm{S}) = \begin{bmatrix} \alpha_3 & \alpha_4 & \alpha_4 \\ \alpha_4 & \alpha_3 & \alpha_4 \\ \alpha_4 & \alpha_4 & \alpha_3 \end{bmatrix}. \tag{24c}$$

All other blocks are derived from (22)–(24) by the symmetry relations (21), (16), and (19). Cubic symmetry in (15) together with the charge neutrality condition (14) further imposes

$$e_{\alpha\beta}(\kappa) = \pm q\,\delta_{\alpha\beta}, \tag{25}$$

where $+q$ is called the *static ionic charge* of the metallic atom ($\kappa = 1$).

Assuming the plane waves

$$u_\alpha(l\kappa\,|\,\vec{k}) = u_\alpha(\kappa\,|\,\vec{k})\,e^{-i\omega t + i\vec{k}\vec{x}(l\kappa)} \tag{26}$$

spread out through the crystal, we may go from $\vec{u}(l\kappa)$, $\vec{p}(l\kappa)$, $\vec{F}(l\kappa)$, and $\vec{E}(l\kappa)$ to the amplitudes, respectively, $\vec{u}(\kappa\,|\,\vec{k})$, $\vec{p}(\kappa\,|\,\vec{k})$, $\vec{F}(\kappa\,|\,\vec{k})$, and $\vec{E}(\kappa\,|\,\vec{k})$, as in (26). Transforming in the usual way also $\Phi_{\alpha\beta}(l\kappa;l'\kappa')$, $m_{\alpha\beta}(l\kappa;l'\kappa')$, and $a_{\alpha\beta}(l\kappa;l'\kappa')$ into their Fourier transforms, respectively, $(M_\kappa M_{\kappa'})^{1/2} \times C^{\mathrm{sr}}_{\alpha\beta}(\kappa\kappa'\,|\,\vec{k})$, $N_{\alpha\beta}(\kappa\kappa'\,|\,\vec{k})$, and $a_{\alpha\beta}(\kappa\kappa'\,|\,\vec{k})$, e.g.,

$$(M_\kappa M_{\kappa'})^{1/2}\,C^{\mathrm{sr}}_{\alpha\beta}(\kappa\kappa'\,|\,\vec{k}) \equiv \sum_{l'-l} \Phi_{\alpha\beta}(l\kappa;l'\kappa')\,e^{i\vec{k}[\vec{x}(l'\kappa')-\vec{x}(l\kappa)]} \tag{27}$$

(see Table I), we may write (20) and (18) in the form

$$\vec{F} = -\underline{M}^{1/2}\,\underline{C}^{sr}\,\underline{M}^{1/2}\vec{u} + (\underline{q} + \underline{N}^\dagger)\,\vec{E}^{\,\mathrm{eff}}, \tag{28a}$$

$$\vec{p} = (\underline{q} + \underline{N})\,\vec{u} + \underline{a}\,\vec{E}^{\,\mathrm{eff}}, \tag{28b}$$

with

$$\vec{E}^{\,\mathrm{eff}} = \underline{B}\,\vec{p}. \tag{28c}$$

Here $\underline{B}$ is the matrix of the Coulomb coefficients[24]; the matrices

$$M_{\alpha\beta}(\kappa\kappa') \equiv M_\kappa\,\delta_{\alpha\beta}\delta_{\kappa\kappa'}\,;\quad q_{\alpha\beta}(\kappa\kappa') \equiv \pm q\,\delta_{\alpha\beta}\delta_{\kappa\kappa'} \tag{29}$$

are, respectively, the matrices of the masses and of the static charges; $\vec{F}$, $\vec{p}$ and $\vec{u}$ are hypervectors with six components $F_\alpha(\kappa)$, $p_\alpha(\kappa)$, and $u_\alpha(\kappa)$; the dagger denotes Hermitian conjugation. Eliminating the electric field, we rewrite (28a) and (28b) as the equations of motion in the variables $\vec{u}$ and $\vec{p}$,

$$\omega^2\,\underline{M}\,\vec{u} = \underline{M}^{1/2}\underline{C}^{sr}\,\underline{M}^{1/2}\vec{u} - (\underline{q} + \underline{N}^\dagger)\underline{B}\,\vec{p}, \tag{30a}$$

$$0 = -\underline{B}(\underline{q} + \underline{N})\,\vec{u} + (\underline{B} - \underline{B}\,\underline{a}\,\underline{B})\,\vec{p}. \tag{30b}$$

Equation (30b) expresses the adiabatic approximation: It may be considered as the equation of motion of the dipole $\vec{p}$ of zero mass. The purpose of the seemingly superfluous multiplication of Eq. (30b) by $-\underline{B}$ was to make equal the coupling term between the displacements and the deformation dipoles in both (30a) and (30b), as is required by microscopic theory.[8] The equality of both terms, which may be visualized as the equality of action and reaction, often remained unnoticed in the previous formulations of the DDM. Finally, eliminating $\vec{p}$ from (30b) we get the equation of motion for the displacement amplitudes $\underline{M}^{1/2}\vec{u}$:

$$\omega^2\,\underline{M}^{1/2}\vec{u} = \underline{C}(\vec{k})\,\underline{M}^{1/2}\vec{u}, \tag{31a}$$

with the dynamical matrix

TABLE I. Short-range part of the dynamical matrix defined by Eq. (27) with the force parameters (22).

$$C^{\mathrm{sr}}_{\alpha\alpha}(\kappa\kappa\,|\,\vec{k}) = -4M_\kappa^{-1}\{A + C_\kappa[2 - c_{2\alpha}(c_{2\beta} + c_{2\gamma})] + F_\kappa(1 - c_{2\beta}c_{2\gamma})\}$$

$$C^{\mathrm{sr}}_{\alpha\beta}(\kappa\kappa\,|\,\vec{k}) = -4M_\kappa^{-1}[D_\kappa s_{2\alpha}s_{2\beta} + (-1)^\kappa i\,E_\kappa s_{2\gamma}(c_{2\alpha} - c_{2\beta})]$$

$$C^{\mathrm{sr}}_{\alpha\alpha}(1,2\,|\,\vec{k}) = +4(M_1M_2)^{-1/2}\,A\,(c_\alpha c_\beta c_\gamma - i\,s_\alpha s_\beta s_\gamma)$$

$$C^{\mathrm{sr}}_{\alpha\beta}(1,2\,|\,\vec{k}) = +4(M_1M_2)^{-1/2}\,B\,(-s_\alpha s_\beta c_\gamma + i\,c_\alpha c_\beta s_\gamma)$$

$$c_\alpha = \cos\tfrac{1}{4}ak_\alpha;\qquad c_{2\alpha} = \cos\tfrac{1}{2}ak_\alpha$$

$$s_\alpha = \sin\tfrac{1}{4}ak_\alpha;\qquad s_{2\alpha} = \sin\tfrac{1}{2}ak_\alpha$$

$$\kappa = 1,2;\qquad \{\alpha,\beta,\gamma\} = \{1,2,3\}$$

$$\underline{C}(\vec{k}) = \underline{C}^{sr}(\vec{k}) - \underline{M}^{-1/2}(\underline{q} + \underline{N}^{\dagger})(\underline{I} - \underline{B}\,\underline{a})^{-1}\underline{B}(\underline{q} + \underline{N})\underline{M}^{-1/2}. \tag{31b}$$

IV. COMPARISON WITH SHELL MODEL

The original version of the Karo-Hardy model was already compared with the shell model (SM) by Cowley *et al.*[25] As the introduction of nonlocal polarizabilities into (18) substantially modifies the former scheme, it will be interesting to see once more whether both models can provide an equivalent description of vibrations, under which conditions the parameters of the deformation-dipole model can be expressed in terms of the shell model, and what the various assumptions on one parameter set mean in the language of the other model.

Let us choose the simplest version of the SM, where all the interactions $\underline{\Phi}^{(R)}$, $\underline{\Phi}^{(S)}$, $\underline{\Phi}^{(T)}$ extend only to first neighbors. This corresponds to the range of the principal interactions (23), (24) in the DDM of Sec. III. The SM is characterized by the ionic charges $Z_1 e = -Z_2 e$, shell charges $Y_1 e$, $Y_2 e$, isotropic core-shell springs k_1, k_2, and by the core-core, shell-shell, and core-shell interactions, which take the form

$$\underline{\Phi}^{(x)}(\mathrm{Zn};\mathrm{S}) = \underline{\Phi}^{(x)}(\mathrm{S};\mathrm{Zn})$$

$$= \begin{bmatrix} A^{(x)} & B^{(x)} & B^{(x)} \\ B^{(x)} & A^{(x)} & B^{(x)} \\ B^{(x)} & B^{(x)} & A^{(x)} \end{bmatrix}, \quad (x) = R, S, T \tag{32}$$

analogous to (22a), (23a), (23b), and (24c). Although the usual notation[7] is $-\alpha^{(x)}$, $-\beta^{(x)}$, we are keeping the symbols $A^{(x)}$, $B^{(x)}$, in analogy with (22a).

The matrices $\underline{R}(\vec{k})$, $\underline{S}(\vec{k})$, $\underline{T}(\vec{k})$ [the Fourier transforms of the coupling parameters (32)] may be easily formed, e.g., with the aid of Table I, and the equations of motion for the Fourier-transformed core displacements $\vec{u}$ and relative shell displacements $\vec{w}$ can be written in the form[7,8]

$$\omega^2 \underline{M}\,\vec{u} = (\underline{R} + \underline{Z}\,\underline{C}\,\underline{Z})\,\vec{u} + (\underline{T} + \underline{Z}\,\underline{C}\,\underline{Y})\,\vec{w}, \tag{33a}$$

$$0 = (\underline{T}^{\dagger} + \underline{Y}\,\underline{C}\,\underline{Z})\,\vec{u} + (\underline{\mathcal{S}} + \underline{Y}\,\underline{C}\,\underline{Y})\,\vec{w}, \tag{33b}$$

which has the same structure as the corresponding equations (30) of the DDM. Here

$$\begin{aligned} Z_{\alpha\beta}(\kappa\kappa') &= Z_{\kappa}\delta_{\alpha\beta}\delta_{\kappa\kappa'} \\ Y_{\alpha\beta}(\kappa\kappa') &= Y_{\kappa}\delta_{\alpha\beta}\delta_{\kappa\kappa'} \end{aligned} \tag{34}$$

are the diagonal matrices of ionic charges and shell charges; $\underline{C}$, standing for the matrix of the Coulomb coefficients, is identical, to within a sign, with the matrix $\underline{B}$ (28c) used in Sec. III,

$$\underline{C}(\vec{k}) = -\underline{B}(\vec{k}), \tag{35}$$

and

$$\begin{aligned} &\underline{\mathcal{S}}_{\alpha\beta}(\kappa\kappa' \,|\, \vec{k}) \\ &\quad \equiv S_{\alpha\beta}(\kappa\kappa' \,|\, \vec{k}) + \delta_{\alpha\beta}\delta_{\kappa\kappa'}[k_{\kappa} + T_{\alpha\alpha}(\kappa\kappa \,|\, \vec{0}) - S_{\alpha\alpha}(\kappa\kappa \,|\, \vec{0})] \end{aligned} \tag{36}$$

(seeRef. 26).

A full equivalence of two models would mean that both models (a) provide the same eigenfrequencies, (b) predict the same displacements of cores (core eigenvectors), and (c) assign the same electric dipoles to the lattice sites. As the dipoles are somewhat fictitious and certainly model-dependent quantities, we are asking in which conditions the SM and DDM will provide an equivalent description of motion of the cores—letting thus aside the question (c). A necessary and sufficient condition for the equality in the points (a) and (b) is the equality of the dynamical matrices in both models.

Eliminating $\vec{w}$ from (33b) we get the dynamical matrix for the core displacements in its usual form,[27] which may be written in an alternative way[28]

$$\begin{aligned} &\underline{M}^{-1/2}[\underline{R} - \underline{T}\,\underline{\mathcal{S}}^{-1}\underline{T}^{\dagger} + (\underline{Z} - \underline{T}\,\underline{\mathcal{S}}^{-1}\underline{Y}) \\ &\qquad \times (\underline{I} + \underline{C}\,\underline{Y}\,\underline{\mathcal{S}}^{-1}\underline{Y})^{-1}\underline{C}\,(\underline{Z} - \underline{Y}\,\underline{\mathcal{S}}^{-1}\underline{T}^{\dagger})]\underline{M}^{-1/2}. \end{aligned} \tag{37}$$

In this form (37) can be directly compared with the dynamical matrix (31b) of the DDM. Sufficient conditions for their equality are written immediately as

$$\underline{a}(\vec{k}) = \underline{Y}\,\underline{\mathcal{S}}^{-1}\underline{Y}, \tag{38a}$$

$$\underline{q} + \underline{N}(\vec{k}) = \underline{Z} - \underline{Y}\,\underline{\mathcal{S}}^{-1}\underline{T}^{\dagger}, \tag{38b}$$

$$\underline{M}^{1/2}\underline{C}^{sr}(\vec{k})\underline{M}^{1/2} = \underline{R} - \underline{T}\,\underline{\mathcal{S}}^{-1}\underline{T}^{\dagger}. \tag{38c}$$

It remains, however, to be seen whether the $\vec{k}$ dependence is the same on both sides of (38).

Inverting (36), we may express the 3×3 blocks of of $\underline{\mathcal{S}}^{-1}(\vec{k})$ in terms of the 3×3 blocks $\underline{S}(\kappa\kappa' \,|\, \vec{k})$ as follows:

$$\begin{aligned} \underline{\mathcal{S}}^{-1}(11 \,|\, \vec{k}) = \{&\underline{S}(11) + k_1'\underline{I}_3 \\ &- \underline{S}(12)[\underline{S}(22) + k_2'\underline{I}_3]^{-1}\underline{S}(21)\}^{-1}, \end{aligned} \tag{39a}$$

$$\underline{\mathcal{S}}^{-1}(21 \,|\, \vec{k}) = -[\underline{S}(22) + k_2'\underline{I}_3]^{-1}\underline{S}(21)\underline{\mathcal{S}}^{-1}(11), \tag{39b}$$

where

$$k_{\kappa}' = k_{\kappa} - 4A^{(T)} + 4A^{(S)} \tag{39c}$$

and the blocks $\underline{\mathcal{S}}^{-1}(22)$, $\underline{\mathcal{S}}^{-1}(12)$ are obtained from (39) by interchanging the labels 1, 2. Formula (39) can be evaluated analytically only in a few particular cases.

Let us first examine the case of an ionic crystal,[29] where

$$k_1, k_2 \gg A^{(S)}. \tag{40a}$$

In the following calculation we shall still keep the terms

$$0 \neq A^{(S)}/k_{\kappa} \ll 1 \tag{40b}$$

and we shall neglect (compared to unity) only the second and higher powers of A/k.

In view of (40), the second term in (39a) may be neglected in comparison to the first one, and we get

$$\underline{\mathcal{S}}^{-1}(11\,|\,\vec{k})=\frac{I_3}{k_1-4A^{(T)}}\,,$$
$$\underline{\mathcal{S}}^{-1}(21\,|\,\vec{k})=\frac{-\underline{S}(21\,|\,\vec{k})}{(k_1-4A^{(T)})(k_2-4A_T^{(T)})}\,, \tag{41}$$

and analogous expressions for $\underline{\mathcal{S}}^{-1}(22)$ and $\underline{\mathcal{S}}^{-1}(12)$. It can be seen now that both sides of Eq. (38a) have the same wave-vector dependence, because both $\underline{a}(\kappa\kappa'\,|\,\vec{k})$ and $S(\kappa\kappa'\,|\,\vec{k})$ were generated from $\underline{a}(l\kappa;l'\kappa')$ or $\underline{\Phi}^{(S)}_{(l\kappa;\,l'\kappa')}$ in the same way. We may therefore compare the individual matrix elements in (38a), and we get

$$\alpha_1=\frac{Y_1^2}{k_1-4A^{(T)}}\,,\quad \alpha_2=\frac{Y_2^2}{k_2-4A^{(T)}}\,, \tag{42a}$$

$$\alpha_3=\frac{-Y_1Y_2}{(k_1-4A^{(T)})(k_2-4A^{(T)})}\,A^{(S)}\,, \tag{42b}$$

$$\alpha_4=\frac{-Y_1Y_2}{(k_1-4A^{(T)})(k_2-4A^{(T)})}\,B^{(S)}. \tag{42c}$$

A similar reasoning allows us to compare both sides of the (12) and (21) blocks in (38b), and to find

$$\gamma_1=\frac{3Y_1A^{(T)}}{k_1-4A^{(T)}}+\frac{12Y_1A^{(S)}A^{(T)}}{(k_1-4A^{(T)})(k_2-4A^{(T)})}\,, \tag{43a}$$

$$\gamma_2=\frac{-3Y_2A^{(T)}}{k_2-4A^{(T)}}-\frac{12Y_2A^{(S)}A^{(T)}}{(k_1-4A^{(T)})(k_2-4A^{(T)})}, \tag{43b}$$

$$\gamma_3=\frac{3Y_1B^{(T)}}{k_1-4A^{(T)}}+\frac{12Y_1B^{(S)}A^{(T)}}{(k_1-4A^{(T)})(k_2-4A^{(T)})}, \tag{43c}$$

$$\gamma_4=\frac{-3Y_2B^{(T)}}{k_2-4A^{(T)}}-\frac{12Y_2B^{(S)}A^{(T)}}{(k_1-4A^{(T)})(k_2-4A^{(T)})}\,. \tag{43d}$$

Before comparing the diagonal (11) and (22) blocks of (38b), let us first recall that, owing to the condition

$$\sum_{\kappa'} N_{\alpha\beta}(\kappa\kappa'\,|\,\vec{0})=0 \tag{44}$$

imposed by (12), the splitting of the left-hand side of (38b) into "charges" and "deformabilities" is unambiguous in the formalism of the DDM. So is the analogous splitting in the formalism of the SM on the right-hand side of (38b), because in the approximation (40) the relation (44) is fulfilled also by the matrix $\underline{Y}\,\underline{\mathcal{S}}^{-1}\,\underline{T}^{\dagger}$, as may be easily verified. We may therefore write

$$\underline{q}=\underline{Z}\quad\text{or}\quad q=Z_1, \tag{45a}$$

$$\underline{N}(\vec{k})=-\underline{Y}\,\underline{\mathcal{S}}^{-1}\,\underline{T}^{\dagger}. \tag{45b}$$

Comparing then the (11) and (22) blocks in (45b), we obtain again (still at $\vec{k}=0$) the relations (43a) and (43b) for γ_1,γ_2; the same comparison at $\vec{k}\neq 0$ leads to a somewhat different $\vec{k}$ dependence of both sides—the difference concerns, however, only the terms of order $(A/k_\kappa)^2$.

We note that the expressions for α_1, α_2 [the diagonal terms in the blocks $\underline{a}(\kappa\kappa\,|\,\vec{k})$] turned out to be identical with those usually denoted as π_1, π_2 in the context of the shell model[30] and we recognize the usual expressions for d_1, d_2 in the (dominating) first term of the expressions for $\frac{4}{3}\gamma_1$, $-\frac{4}{3}\gamma_2$ [the diagonal terms in the blocks $\underline{N}(\kappa\kappa\,|\,\vec{k})$].

Summing up, the influence of polarization effects on core motion, characterized in the shell model by the eight parameters

$$A^{(S)},\ B^{(S)},\ A^{(T)},\ B^{(T)},\ k_1,\ k_2,\ Y_1,\ Y_2 \tag{46}$$

can be reproduced by the DDM formalism if we relate its eight parameters

$$\gamma_1,\ldots,\gamma_4,\quad \alpha_1,\ldots,\alpha_4 \tag{47}$$

to the parameters (46) by formulas (42) and (43). Moreover, we can see from (42) that the first-neighbor SM attributes to the nonlocal polarizabilities (24c) small but nonvanishing values of order A/k times the local polarizabilities $\underline{a}(l\kappa;l\kappa)$. In the shell model, as a consequence of (19b) and (42), if one assumes that only one ion is polarizable (e.g., $k_1\to\infty$) all nonlocal polarizabilities vanish. This apparently unphysical limitation does not exist in the formalism of the DDM; in the numerical calculations, however, it can hardly have any noticeable effect, as long as the SM is applied to ionic crystals, in which case condition (40) holds.

Having established the equivalence of both languages, we may ask what the different assumptions about one model mean in the language of the other one; e.g., the assumption, frequent in SM calculations, that the interactions are transmitted only through the shells ($\underline{R}=\underline{S}=\underline{T}$) can be formulated in the DDM with the aid of (43) as

$$\gamma_1:\gamma_2=\gamma_3:\gamma_4=-Y_1/k_1:Y_2/k_2\,, \tag{48}$$

$$\gamma_1:\gamma_3=\gamma_2:\gamma_4=A^{(T)}:B^{(T)}. \tag{49}$$

On the other hand, neglecting the nonlocal electric polarizabilities (42b) and (42c) in the DDM (i.e., the Karo-Hardy model) would impose on the shell model the condition

$$A^{(S)}=B^{(S)}=0,$$

i.e.,

$$\Phi^{(S)}=0, \tag{50}$$

that is, shell-shell interactions would be entirely neglected.

The last matrix to be examined is the short-range part of the dynamical matrix. Evaluating, e.g., the (12) block on both sides of (38c), we get

$$\begin{aligned}(M_1M_2)^{1/2}\underline{C}^{sr}(12) = \underline{R}(12) &- \underline{T}(11)\underline{s}^{-1}(11)\underline{T}^{\dagger}(21)\\ &- \underline{T}(12)\underline{s}^{-1}(22)\underline{T}^{\dagger}(22)\\ &- \underline{T}(11)\underline{s}^{-1}(12)\underline{T}^{\dagger}(22)\\ &- \underline{T}(12)\underline{s}^{-1}(21)\underline{T}^{\dagger}(21), \qquad (51)\end{aligned}$$

which shows that the short-range forces appearing in the DDM need not necessarily be identical with the core-core interactions of the shell model. The last two terms in (51) may be neglected against $\underline{R}(12)$ in view of (40); the remaining terms have the same $\vec{k}$ dependence on both sides of (51) because $\underline{T}(\kappa\kappa)$ and $\underline{s}^{-1}(\kappa\kappa)$ are diagonal, and their comparison gives

$$A = A^{(R)} + 4A^{(T)2}\left(\frac{1}{k_1 - 4A^{(T)}} + \frac{1}{k_2 - 4A^{(T)}}\right), \qquad (52a)$$

$$B = B^{(R)} + 4A^{(T)}B^{(T)}\left(\frac{1}{k_1 - 4A^{(T)}} + \frac{1}{k_2 - 4A^{(T)}}\right). \qquad (52b)$$

Thus the short-range matrices in both models differ only by terms of first order in A/k.

Finally, let us examine how the preceding reasoning is to be modified in the case of a covalent crystal[29] when the assumption (40) has to be relaxed. It is instructive to examine first the short-range forces. The matrices $s^{-1}(11)$ and $s^{-1}(22)$ possess now a small $\vec{k}$-dependent nondiagonal contribution, and if we write down, e.g., the (11) block of (38c),

$$\begin{aligned}M_1\underline{C}^{sr}(11) = \underline{R}(11) &- \underline{T}(11)\underline{s}^{-1}(11)\underline{T}^{\dagger}(11)\\ &- \underline{T}(11)\underline{s}^{-1}(12)\underline{T}(21)\\ &- T(12)\underline{s}^{-1}(22)\underline{T}^{\dagger}(12), \qquad (53)\end{aligned}$$

we can see that an exact comparison is impossible: The matrix $\underline{C}^{sr}(11)$ is diagonal and wave-vector independent—if only first-neighbor interactions are considered—while the right-hand side of (53) depends on $\vec{k}$. Accounting for second-neighbor interactions in the DDM, we can get a nondiagonal contribution to $\underline{C}^{sr}(11)$ which will also depend on $\vec{k}$, but not in the same way as the terms on the right-hand side of (53). We may then view the $\vec{k}$-dependent terms on the left-hand side as only *simulating* the $\vec{k}$ dependence of the right-hand side of (53): the first-neighbor shell-shell and core-shell interactions of the shell model have thus built up the effective second-neighbor forces of the deformation-dipole model.

It should be noted that our comparison of a second-neighbor DDM with a first-neighbor *SM* is somewhat accidental. Vice versa, if we compared

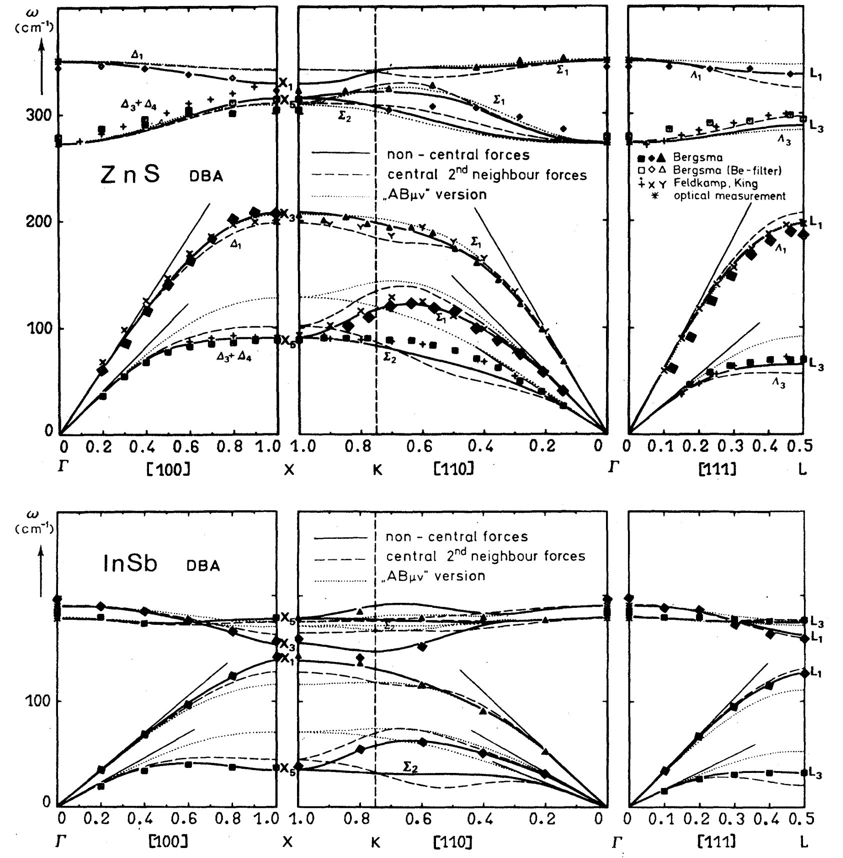

FIG. 1. Dispersion curves of ZnS and InSb calculated using the 15-parameter version of the DDM (solid lines) compared to neutron and optical measurements of phonon frequencies (Refs. 29(a) and 31–35 for ZnS, and Ref. 36 for InSb). Various stages in the process of determination of parameters lead to simplified models which are represented by broken and dotted lines (second-neighbor central forces and central springs, respectively). The results of similar calculations for ZnSe, GaP, GaAs, SiC, CuCl, and CuI are given in Ref 4.

a first-neighbor DDM with the second-neighbor SM, we would have to conclude, by the same reasoning, that the second-neighbor contribution to $\underline{R}(11)$ simulates the wave-vector-dependent part of $M_1\underline{C}^{sr}(11)+(\underline{T}\,\underline{S}^{-1}\underline{T}^{\dagger})(11)$ produced by mere first neighbors in the DDM. In the absence of any corresponding numerical evaluations of the first- and second-neighbor versions of both models, the two interpretations above are *a priori* plausible and we cannot decide whether the $\underline{T}\,\underline{S}^{-1}\underline{T}^{\dagger}$ term in (38c) is missing in the DDM or it contributes in excess in the SM.

As for the polarizabilities and deformabilities, the relaxing of (40) will produce a similar effect: The matrix $\underline{a}(11|\vec{k})$ will turn out to be nondiagonal and the $\vec{k}$ dependence of $\underline{N}(12|\vec{k})$ will no longer correspond exactly to that of $(-\underline{Y}\,\underline{S}^{-1}\underline{T}^{\dagger})$ (12). Again, we could *simulate* this modification by introducing the second-neighbor polarizabilities and deformabilities. The conclusion of the last paragraph nevertheless applies also to this case.

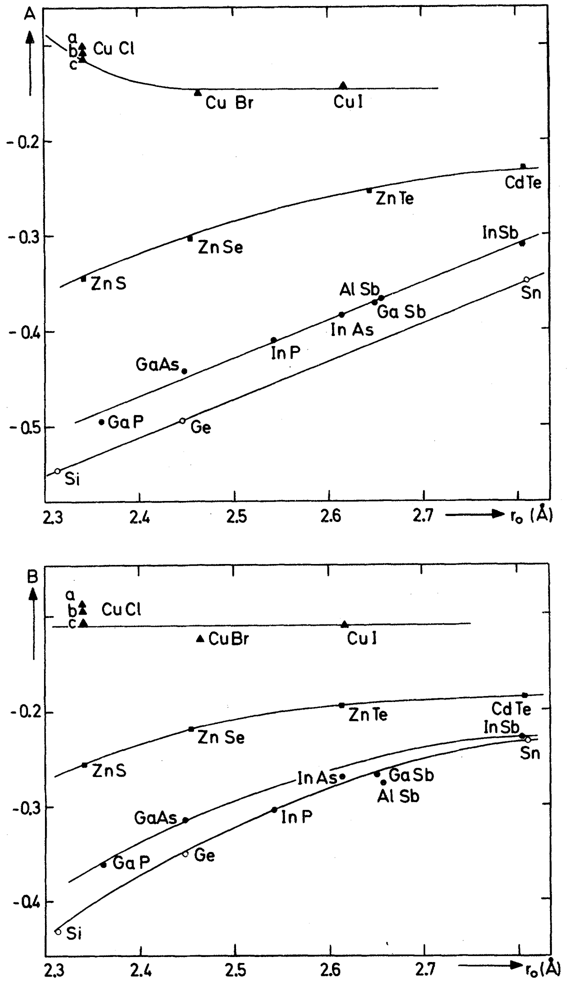

FIG. 2. Some of the fitted model parameters may be organized into regular schemes. For every group of compounds (II-VI, III-V, etc.) the parameters A, B characterizing the short-range interaction between first neighbors [eq. (22a)] vary as monotonic functions of interatomic distance r_0. These regularities are discussed in more detail in Ref. 5.

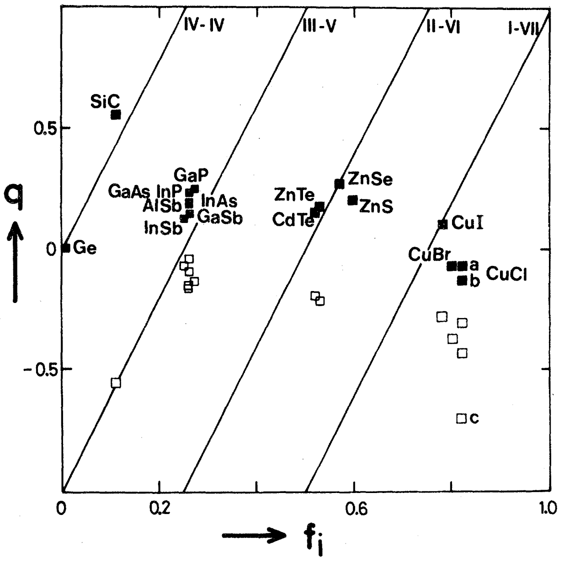

FIG. 3. For every group of compounds (II-VI, III-V, etc.) the static ionic charge q [Eq. (25)] is approximately the linear function (57) of the ionicity f_i (straight lines). As the procedure for determining q provided two values for each compound, every material is characterized by one full and one open square, the latter being considered as unphysical. The above regular behavior was found only when the ionicity scale of Pauling was used. See Ref. 5 for a more detailed discussion.

We may thus conclude that both models seem to provide different descriptions of those covalent crystals in which condition (40) does not hold—in contrast to ionic crystals, where the equivalence of the SM and DDM was shown. An exact analysis, following the lines of the Eqs. (41)–(52), is hard to perform in the covalent case, because the $\underline{S}^{-1}$ matrix cannot be written down explicitly for $\vec{k}\neq 0$. The comparison which we have made in this case, at least for $\vec{k}=0$, provided expressions for γ_1, γ_2, α_1, α_2 and α_3 of a form analogous to formulas (42) and (43): The ratio of local and nonlocal polarizabilities was again found to be of order k/A—which suggests that the nonlocal polarizabilities may play as important role as the local ones in covalent crystals. Numerical comparison of both models in the case of covalent crystals would therefore be desirable—unfortunately, the DDM has never been applied in its full generality.

V. SOME NUMERICAL RESULTS

In addition to the Karo-Hardy approximation

$$\underline{a}(l\kappa;l'\kappa')=0 \quad \text{for } (l\kappa)\neq(l'\kappa'), \tag{54a}$$

i.e.,

$$\alpha_3=\alpha_4=0, \qquad (54b)$$

we have assumed in the computations that

$$\gamma_3=\gamma_1, \quad \gamma_4=\gamma_2, \qquad (55)$$

and call (54) with (55) the deformable-bond approximation (DBA). This approximation has been applied with success to the lattice dynamics of[23a,b] CdS and BeO and its physical significance is discussed in detail in Ref. 1. In the language of the shell model the assumption (55) means that

$$A^{(T)}\approx B^{(T)}, \qquad (56)$$

as is readily seen from Eq. (43). Equation (56) is equivalent to the assumption of central *springs* between first-neighbor cores and shells if the equality holds exactly. (This is the case only when it is assumed either that $\underline{S}=\underline{T}$, or that $\underline{S}=0$.)

Thus we have arrived at a 15-parameter model, which we have applied to 15 different compounds of the A^NB^{8-N} type having the zinc-blende structure.[4] A complete set of parameters could, however, only be determined for eight compounds—those for which the neutron measurements of phonon frequencies existed: ZnS, ZnSe, GaP, GaAs, InSb, SiC, CuCl, and CuI. As for the remaining seven compounds, it was possible to calculate only certain combinations of parameters from which, nevertheless, certain qualitative conclusions can be drawn. We reproduce in Fig. 1 the dispersion curves obtained for ZnS and InSb, which are chosen as typical examples of rather ionic and rather covalent structures, respectively. The analogous curves calculated for all other compounds studied may be found in Ref. 4, where they are compared with the results of the 11-parameter rigid-ion models.

As we wished to obtain model parameters which would not only provide an interpolation scheme for phonon frequencies but would also be physically meaningful, particular care was taken in the development of an appropriate method for fitting these parameters to experimental data. The idea of the procedure[4] is to decompose the fitting process into several steps corresponding to different degrees of simplification of the model. Proceeding from simpler to more complicated versions, we fit (suitably chosen) groups of parameters or combinations of parameters to neutron data and to macroscopic quantities (elastic, piezoelectric, and dielectric constants) alternatively, trying at every step to maintain continuity with the preceding stage. The broken and dotted lines of Fig. 1 correspond to two of the intermediate results of this algorithm: one, a model where second-neighbor forces were derived from a central two-body potential, and the other, a model where these forces were represented by harmonic springs only.

The degree of success of this method for determination of parameters can be judged from Figs. 2 and 3, where some of the parameters obtained in this way are represented graphically. It can be seen from Fig. 2 that short-range forces between first neighbors (parameters A, B) vary as monotonic functions of interatomic distance r_0. The static ionic charge q of an A^NB^{8-N} compound plotted in Fig. 3 as a function of ionicity f_i approximately satisfies the relation derived in Ref. 5,

$$q=[N+4(f_i-1)]\,e\,. \qquad (57)$$

The reader is referred to this reference for the description of some other trends, as well as for a more detailed discussion of Figs. 2 and 3. The possibility of organizing the fitted model parameters into a regular scheme is probably a more significant result of the present work than the successful fitting of all the experimental data by the model.

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[14] Let us recall that in the most general case the linear material-equations of the macroscopic electrodynamics are to be written in the nonlocal form $D_i(\vec{r}, t) = \sum_j \int\int \epsilon_{ij}(\vec{r}, \vec{r}', t, t') E_j(\vec{r}', t') d\vec{r}' dt'$, or, alternatively, $D_i(\omega, \vec{k}) = \sum_j \epsilon_{ij}(\omega, \vec{k}) E_j(\omega, \vec{k})$; see, e.g., V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Interscience, London, 1966), pp. 3–4.

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[29] Typical values for an ionic crystal: $k_1=\infty$, $k_2=71.4$ e^2/v, $A^{(R)}=A^{(S)}=-2.96$ $e^2/2v$ in NaCl. {See J. S. Reid [Phys. Status Solidi B 48, 591 (1971)], Table 1; for other alkali halides the ratio A/k is still smaller.} Typical values for a covalent crystal: $k_1=k_2=93.4$ e^2/v, $A^{(S)}=-35.05$ e^2/v in Ge [G. Dolling and R. A. Cowley, Proc. Phys. Soc. Lond. 88, 463 (1966)]. Note, however, that this ionic-covalent distinction, based on (40a), is largely model dependent: Comparing the shell models actually available for zinc-blende-structure compounds [(a) N. Vagelatos, D. Wehe, and J. S. King, J. Chem. Phys. 60, 3613 (1974); (b) D. L. Price, J. M. Rowe, and (c) R. M. Niklow, Phys. Rev. B 3, 1268 (1971), Table III.], we find that (40a) is satisfied best for Sn (*sic*) with $A^{(S)}/k=0.03$. The values of $A^{(S)}/k(\kappa)$ for ZnS and ZnTe vary from 0.005 to 0.11, according to the model and to whether κ stands for Zn or for S; we get acceptable ionic-like values in (40a) even for InSb and diamond [$A^{(S)}/k(\mathrm{In})=0.096$, $A^{(S)}/k(\mathrm{Sb})=0.047$, $A^{(S)}/k(\mathrm{C})=0.11$]. Only the models for Si, GaAs, Ge, and GaP do not fall into the ionic case, their $A^{(S)}/k$ being, respectively, 0.25, ≤ 0.27, 0.38, and ≤ 0.64.

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