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Bond-deformation model for rocksalt-structure compounds

A. L. Dragoo
National Measurement Laboratory, National Bureau of Standards, Washington, D.C. 20234

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The bond-deformation model is developed for compounds having the rocksalt structure—namely, the alkali halides and the alkaline-earth oxides. The full set of nearest-neighbor bond-deformation parameters is presented, and the parameters are related to the Lagrangian and internal strains and to the atomic displacements. The next-nearest-neighbor bond-stretching parameters are shown to be reducible to the nearest-neighbor parameters. A variety of central-force and non-central-force interactions is identified in the expansion of the short-range portion of the strain energy. By a transformation of variables the short-range contributions to the dynamical matrix are obtained. Expressions are derived for the elastic constants and for the force constant associated with the homogeneous polarization of the lattice.

I. INTRODUCTION

The interactions between ions in a crystal are generally assumed to consist of a long-range electrostatic interaction and of one or more short-range and intermediate-range interactions. These latter interactions may derive from overlap repulsions of closed electronic shells on adjacent ions, from van der Waals interactions, and from covalent bonding. The high symmetry and simple crystal structure of ionic compounds with the rocksalt structure—that is, the alkali halides and the alkaline-earth oxides—facilitate theoretical treatments of these interactions. Moreover, reliable experimental data for these compounds permit theoretical models to be tested.

The long-range interaction and a large part of the short-range interactions in ionic compounds can be treated as central-force (CF) interactions between pairs of atoms. Nevertheless, it is found empirically—for example, by the fact that the elastic constants C_{12} and C_{44} are not equal—that many-body (MB) or noncentral-force (NCF) interactions[1] are present in these materials. Consequently, a variety of models of these interactions, usually in a three-body approximation, has been introduced into descriptions of ionic bonding: charge-transfer models,[2,3] angle-bending models,[4–6] a multiple bond-stretching model,[7] deformable shell models,[8–10] multipole models,[11,12] and triple-dipole models.[13–15] The number of NCF coefficients introduced into the overall ionic bonding model must be limited by the necessity of evaluating all of the coefficients from the experimental data.

In this paper this restriction of the number of empirical coefficients will be relaxed for the moment so that the variety of possible short-range interactions can be examined. A large set of phenomenological coupling constants will be obtained which will describe all of the nearest-neighbor (NN) bond interactions and many of the next-nearest-neighbor (NNN) bond interactions for the complex of atoms shown in Fig. 1(a). This complex consists of a fiducial central atom, which may be on either sublattice in the case of the rocksalt structure, and its six NN ions on the opposite sublattice. Changes in length of individual NN bonds, shown in Fig. 1(a), and of NNN bonds, shown as the heavy solid lines in Fig. 1(b), constitute the short-range CF interactions. NCF interactions involve deformation of one or more bond angles, coupled changes of different bond lengths, and coupled deformation of bond angles and bond lengths. It is apparent that NCF interactions may be complicated even for structures as simple as that for rocksalt.

The formalism of the bond-deformation model (BDM) offers a convenient means for obtaining a phenomenological description of the short-range interactions in the complex of atoms shown in Fig. 1. The BDM was introduced by Keating[16] as a microscopic description of elastic strain in crystals having the diamond structure. The bond-deformation parameters of his model are scalar quantities which are easily related to components of the Lagrangian strain. An expansion of the strain energy in powers of these parameters is rotationally invariant. Keating spe-

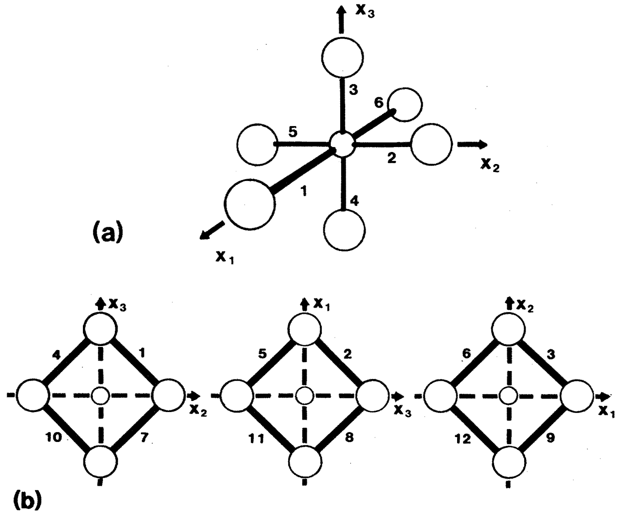


FIG. 1. Arrangement of atoms in a NN complex in the rocksalt structure. (a) Labeling scheme for NN bonds. (b) Labeling scheme for NNN bonds.

cialized the BDM to a case of two coupling constants: a bond-stretching constant and a bond-bending constant. Martin[17] applied Keating's model to an analysis of the elastic constants of zinc-blende—structure semiconductors. Fuller[18] used an expanded set of coupling constants to derive the second- and third-order elastic constants for CdS. Dragoo[6] applied the BDM to an analysis of NN noncentral-force interactions in the alkaline-earth oxides. The treatment of the BDM given here expands the earlier work on the alkaline-earth oxides, in particular, by demonstrating that NNN CF interactions are included in the BDM and by showing how a formulation of lattice dynamics can be obtained from the BDM.

Once the phenomenological coupling constants are identified, we proceed toward obtaining a properly constrained model—that is, a model in which no coupling constants remain undetermined. As a first step, constraints required by symmetry and equilibrium are imposed to obtain a reduced set of independent coupling constants. Further constraints which are needed to obtain the requisite number of BDM coupling constants must be introduced as heuristic conditions or from microscopic models of the interactions. However, as will be shown in this work, it is not necessary to specify all of the required constraints before ideas about the NCF contributions to ionic bonding can be obtained.

This paper presents the formal development of the BDM. In Sec. II the bond-deformation parameters are introduced and are related to the atomic displacements and to the Lagrangian and internal strains. These parameters are defined first according to Keating,[16] but a very useful set of transformed parameters also is given. The strain energy is expanded in the bond-deformation parameters in Sec. III. The coefficients of this expansion, the "coupling constants," are analyzed in detail. In Sec. IV certain NNN interactions are shown to be contained in the description given by the full set of NN bond-deformation parameters and coupling constants. The central-force contributions to the coupling constants are examined in Sec. V. In Sec. VI an expansion of the strain energy in the transformed bond-deformation parameters is used to provide the basis for deriving the short-range force constants required for the lattice dynamics of rocksalt-type compounds. In Sec. VII expressions are obtained for the elastic constants and for the force constant associated with the homogeneous polarization of the lattice.

NCF contributions to these empirical coefficients are compared, and it is shown that the NCF contributions to the inequality of C_{12} and C_{44} and to the force constant for homogeneous polarization of the lattice do not necessarily derive from a single NCF interaction.

II. THE BOND-DEFORMATION PARAMETERS

In contrast to the customary formulation of lattice dynamics—for example, Born and Huang[19] and Maradudin *et al.*[20]—the BDM emphasizes the changes in bond lengths and bond angles, collectively called "bond deformations" here, rather than the displacements of the atoms themselves. For the compound *AB* the bond-deformation parameter

$$\lambda(\alpha,\beta;\nu)=[\vec{r}\,'(\alpha,\nu)\cdot\vec{r}\,'(\beta,\nu)-\vec{r}(\alpha,\nu)\cdot\vec{r}(\beta,\nu)]/\Omega_o^{1/3} \tag{2.1}$$

describes the deformation of the bonds α and β about the central atom ν. The index ν identifies the central-atom site (l,κ) where in the notation of Born and Huang l is the cell index and κ is the basis index. Since the terminal atoms of the NN bonds and the central atom are on different sublattices, the index of a terminal atom uniquely specifies its NN bond to the central atom. Frequently it is sufficient to identify the central atom only with respect to its type (for example, $+$, $-$, or A,B), in which case the appropriate designation will be used for ν. A labeling scheme for the NN bonds is given in Fig. 1(a). The indices α and β run over numerical values from 1 to 6. The numbering of the bonds is ordered so that

$$\alpha+\bar{\alpha}=7\ , \tag{2.2}$$

where the complement, $\bar{\alpha}$, of α labels the bond on the reverse side of the central atom. An alternative numbering scheme in which $\alpha,\beta,\ldots=1$—3 and $\bar{\alpha},\bar{\beta},\ldots=4$—6 will be used as required.

For atom α its equilibrium position with respect to the central atom is $\vec{r}(\alpha,\nu)$; its displaced position is $\vec{r}\,'(\alpha,\nu)$

$$\vec{r}\,'(\alpha,\nu)=\vec{r}(\alpha,\nu)+\vec{u}(\alpha,\nu)\ , \tag{2.3}$$

where

$$\vec{u}(\alpha,\nu)=\vec{u}(\alpha)-\vec{u}(\nu) \tag{2.4}$$

is the displacement of atom α with respect to that of atom ν. The equilibrium angle between bonds α and β is θ; θ' is the angle after a displacement of the bonds. The volume per atom is

$$\Omega_o=\tfrac{1}{2}\Omega_c=a^3\ , \tag{2.5}$$

where Ω_c is the volume of the unit cell for one formula unit *AB*, and $a=|\vec{r}(\alpha,\nu)|$.

Since in the *AB* compounds having the rocksalt structure both *A*- and *B*-type atoms have the same coordination, the sets of bond-deformation parameters associated with the two sublattices are formally similar. Where the designation on the central atom is not required for clarity, it will be ignored for convenience.

Although $\lambda(\alpha,\beta;\nu)$ is a scalar quantity in Cartesian space, it can be viewed as a component of a symmetric 6×6 tensor in the space defined by the six NN bonds. The relationship between the bond-deformation tensor $\underline{\Lambda}$ and the Lagrangian strain tensor will be given later in this section. The bond-deformation tensor can be decomposed into three tensors as follows:

(1) bond-stretching tensor $\underline{\Lambda}_S$:

$$\lambda(\alpha,\alpha)=\{[r'(\alpha)]^2-[r(\alpha)]^2\}/a,\quad \alpha=\beta \tag{2.6a}$$

(2) axial-stretching tensor $\underline{\Lambda}_A$:

$$\lambda(\alpha,\bar{\alpha})=[r'(\alpha)r'(\bar{\alpha})\cos\theta'+r(\alpha)r(\bar{\alpha})]/a\ ,\quad \theta=180° \tag{2.6b}$$

(3) bond-bending tensor $\underline{\Lambda}_B$:

$$\lambda(\alpha,\beta)=r'(\alpha)r'(\beta)\cos\theta'/a,\quad \theta=90^\circ\ . \tag{2.6c}$$

There are 36 bond-deformation parameters associated with each central atom; only 15 of these parameters are required to specify fully the displacements of the six NN bonds if rotations of the complex are excluded.

The bond-stretching tensor $\underline{\Lambda}_S$ has nonzero components along its major diagonal. These components $\lambda(\alpha,\alpha)$ describe the dilation of the six NN bonds. From the labeling scheme in Fig. 1(a) it is evident that

$$\lambda(\alpha,\alpha;A)=\lambda(\bar{\alpha},\bar{\alpha};B)\ . \tag{2.7}$$

The axial-stretching tensor $\underline{\Lambda}_A$ has the components $\lambda(\alpha,\bar{\alpha})$ along its minor diagonal which describe the changes of the three axial lengths through the central atom. These parameters also include the change in the 180° angle between pairs of bonds on opposite sides of the central atom. Since $\lambda(\alpha,\alpha)$ and $\lambda(\alpha,\bar{\alpha})$ are similar, it will be convenient to include $\underline{\Lambda}_A$ with $\underline{\Lambda}_S$ in this model.

The bond-bending tensor $\underline{\Lambda}_B$ is symmetric, $\lambda(\alpha,\beta)=\lambda(\beta,\alpha)$, with 0's along both the major and minor diagonals. Thus of the 24 bond-bending parameters 12 are specified by symmetry. Requiring that NN and NNN bonds remain coherent after a deformation specifies six more of the bond-bending parameters. With the use of the six bond-stretching parameters, the three axial-stretching parameters and six of the bond-bending parameters, the 15 bond-deformation parameters are obtained, which are needed to describe the deformation of the complex in Fig. 1(a).

To relate the BDM to conventional CF models which include NNN displacements, it is desirable to show that the NN bond-deformation parameters contain the NNN bond-stretching parameters. A labeling scheme for these bonds is given in Fig. 1(b). The bond-stretching parameters for these bonds can be specified in terms of the bond index $\epsilon=1-12$ as $\lambda'(\epsilon,\epsilon;\nu)$, or in terms of the atom pairs as $\lambda'(\alpha,\alpha;\beta)$. Since NNN atoms are on the same sublattice, either atom may be taken as the reference atom, thus

$$\lambda'(\alpha,\alpha;\beta)=\lambda'(\beta,\beta;\alpha)\ . \tag{2.8}$$

There are 24 parameters if the NNN bond-stretching parameters are specified with respect to the atom pairs, such that both types of parameters appearing in Eq. (2.8) are counted, but parameters with crossed indices—for example, $\lambda(\alpha,\beta;\beta)$—are not counted.

The bond notation is convenient for counting the interactions of the NNN bonds and will be used in Sec. IV, where the NNN portion of the strain energy is treated in detail. The atom-pair notation will be used in this section to define the NNN bond-stretching parameters and to obtain a reduction of these parameters to the NN bond-deformation parameters. We define the NNN bond-stretching parameters as

$$\lambda'(\alpha,\alpha;\beta)=\{[r'(\alpha,\beta)]^2-[r(\alpha,\beta)]^2\}/a\ , \tag{2.9}$$

where $\vec{r}(\alpha,\beta)$ and $\vec{r}\,'(\alpha,\beta)$ refer to the undeformed and deformed NNN bonds, respectively.

The dependence of the NNN bond-stretching parameters on the NN bond-deformation parameters follows from the law of cosines. For a triad of atoms designated according to the following scheme

Central (apex) atom	Bond atoms	
1	2	3
2	3	1
3	1	2

the bond-deformation parameters obey the relationship

$$\lambda'(\alpha,\alpha;\beta)=\lambda(\alpha,\alpha;\nu)+\lambda(\beta,\beta;\nu)-2\lambda(\alpha,\beta;\nu)\ , \tag{2.10}$$

where the bond-stretching parameter on the left of the equality can be taken to be a NNN parameter while those on the right can be identified with the NN parameters.

Although the bond-deformation parameters can be extended to neighbors of any degree of remoteness, this method is unwieldy. Since all unit cells are considered to be equivalent, it is formally simpler to restrict the bond-deformation parameters to the NN parameters. Interactions involving atoms more remote than those associated with NN bonds are then handled through the coupling constants, which will be discussed in the next section.

It is convenient to introduce a new set of bond-deformation parameters, $\{\mu\}$. These parameters can be shown to be related simply to the relative atomic displacements given by Eq. (2.4). The μ parameters are obtained by the tensor transformation

$$\mu(\alpha,\beta)=a_{\alpha\epsilon}a_{\beta\xi}\lambda(\epsilon,\xi)\ , \tag{2.11}$$

where

$$\underline{a}=\begin{bmatrix} \frac{1}{2} & 0 & 0 & 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2}i & \frac{1}{2}i & 0 & 0 \\ 0 & -\frac{1}{2}i & 0 & 0 & \frac{1}{2}i & 0 \\ -\frac{1}{2} & 0 & 0 & 0 & 0 & \frac{1}{2}i \end{bmatrix} \tag{2.12}$$

is the array of transformation coefficients. The transformed parameters form a bond-stretching tensor $\underline{M}_S$ and a bond-bending tensor $\underline{M}_B$.

The atomic description of homogeneous strains—see Born and Huang,[19] Chap. III—can be used to express the bond-deformation parameters in terms of the Lagrangian strain components, $\{\eta_{ij}:\ i,j=1,2,3\}$, and to the internal strain components, $\{w_i:\ i=1,2,3\}$ through the transformation of the displaced atomic positions to the undisplaced positions. The Cartesian components, $\{x_i'\}$, of the position vector for the displaced position can be expressed in terms of the components of the undisplaced position by the transformation

$$x_i'(\alpha,\nu)=J_{ij}x_j(\alpha,\nu)\pm w_i a\ , \tag{2.13}$$

where summation over repeated indices is implied. The transformation coefficients $\{J_{ij}\}$ are given by

$$J_{ij}=\left.\frac{\partial x_i'}{\partial x_j}\right|_0 . \tag{2.14}$$

The internal strain

$$\vec{w}=[\vec{u}(B)-\vec{u}(A)]/a \tag{2.15}$$

is defined so that the sign before the second term on the right-hand side of Eq. (2.13) is "+" if $\nu=A$ and "−" if $\nu=B$. Following Born and Huang, we define a new internal strain $\bar{w}$, whose components are given by

$$\bar{w}_i=J_{ji}w_i . \tag{2.16}$$

The η_{ij} component of the Lagrangian strain is given by

$$\eta_{ij}=\tfrac{1}{2}(J_{ki}J_{ki}-\delta_{ij}) . \tag{2.17}$$

Substituting Eq. (2.13) into Eq. (2.1) and rewriting the result in terms of the strains yields

$$\lambda(\alpha,\beta;\nu)=2\eta_{mn}x_m(\alpha,\nu)x_n(\beta,\eta)/a \pm\bar{w}_n[x_n(\alpha,\nu)+x_n(\beta,\nu)]+(\bar{w})^2a . \tag{2.18}$$

Since atoms on either sublattice undergo similar displacements, it is convenient to sum the bond-deformation parameters over ν to obtain symmetric and asymmetric unit-cell bond-deformation parameters

$$\lambda(\alpha,\beta)=[\lambda(\alpha,\beta;A)+\lambda(\alpha,\beta;B)]/2 , \tag{2.19a}$$

$$\bar{\lambda}(\alpha,\beta)=[\lambda(\alpha,\beta,A)-\lambda(\alpha,\beta;B)]/2 . \tag{2.19b}$$

For homogeneous deformations $\lambda(\alpha,\beta)$ and $\bar{\lambda}(\alpha,\beta)$ become

$$\lambda(\alpha,\beta)=2\eta_{mn}x_m(\alpha,A)x_n(\beta,A)/a+(\bar{w})^2a , \tag{2.20a}$$

$$\bar{\lambda}(\alpha,\beta)=\bar{w}_n[x_n(\alpha,A)+x_n(\beta,A)] . \tag{2.20b}$$

With the use of Eqs. (2.11), (2.12), and (2.18), the parameters $\mu(\alpha,\beta;\nu)$ can be expressed in the strains. We give here the unit-cell bond-deformation parameters.

$$\mu(\alpha,\beta)=(\bar{w})^2a , \tag{2.21a}$$

$$\bar{\mu}(\alpha,\beta)=-i\bar{w}_nx_n(\beta,A) , \tag{2.21b}$$

$$\bar{\mu}(\bar{\alpha},\beta)=-i\bar{w}_nx_n(\alpha,A) , \tag{2.21c}$$

$$\mu(\alpha,\beta)=-2\eta_{mn}x_m(\alpha,A)x_n(\beta,A)/a , \tag{2.21d}$$

where $\alpha,\beta=1$–3; $\bar{\alpha},\bar{\beta}=4$–$6$. The remaining parameters can be shown to vanish. Useful derivatives of $\lambda(\alpha,\beta;\nu)$ and $\mu(\alpha,\beta;\nu)$ with respect to the atomic displacements, strains, bond lengths, and bond angles are given in Appendix A.

III. COUPLING CONSTANTS

Keating[16] wrote the expansion of the strain energy $\mathscr{V}$ in powers of λ for diamond in a very general way [see his Eq. (6)] but retained only those terms involving deformations of bonds about a single atom. He further restricted the series by ignoring all cross terms. Fuller[18] expanded the strain energy for CdS in a similar way but included some cross terms. Fuller's notation is adapted here to the rocksalt structure. The expansion of the strain energy is

$$\mathscr{V}=f(\alpha,\beta;\nu)w_{\alpha\beta}\lambda(\alpha,\beta;\nu)+\tfrac{1}{2}f(\alpha,\beta;\gamma,\delta;\nu)w_{\alpha\beta}w_{\gamma\delta}\lambda(\alpha,\beta;\nu)\lambda(\gamma,\delta;\nu)+\cdots , \quad \alpha,\beta,\ldots=1\text{–}6,\ \nu=A,B . \tag{3.1}$$

Summation over repeated indices, including ν, is implied. The parameters $w_{\alpha\beta}$ are weights which have the following values: for bond stretching, $w_{\alpha\alpha}=1$; for axial stretching, $w_{\alpha\bar{\alpha}}=\frac{1}{2}$; for bond bending, $w_{\alpha\beta}=\frac{1}{4}$. These weights compensate for double counting of interactions.

The summation over ν can be carried out formally by using the following definitions for effective unit-cell coupling constants:

$$f(\alpha,\beta)=w_{\alpha\beta}[f(\alpha,\beta;A)+f(\alpha,\beta;B)] , \tag{3.2a}$$

$$\bar{f}(\alpha,\beta)=w_{\alpha\beta}[f(\alpha,\beta;A)-f(\alpha,\beta;B)] , \tag{3.2b}$$

$$f(\alpha,\beta;\gamma,\delta)=w_{\alpha\beta}w_{\gamma\delta}[f(\alpha,\beta;\gamma,\delta;A)+f(\alpha,\beta;\gamma,\delta;B)] , \tag{3.2c}$$

$$\bar{f}(\alpha,\beta;\gamma,\delta)=w_{\alpha\beta}w_{\gamma\delta}[f(\alpha,\beta;\gamma,\delta;A)-f(\alpha,\beta;\gamma,\delta;B)] . \tag{3.2d}$$

Employing these definitions in Eq. (3.1) yields to second order

$$\begin{aligned}\mathscr{V}={}&f(\alpha,\beta)\lambda(\alpha,\beta)+\bar{f}(\alpha,\beta)\bar{\lambda}(\alpha,\beta)\\&+\tfrac{1}{2}f(\alpha,\beta;\gamma,\delta)[\lambda(\alpha,\beta)\lambda(\gamma,\delta)+\lambda(\alpha,\beta)\lambda(\gamma,\delta)]\\&+\tfrac{1}{2}\bar{f}(\alpha,\beta;\gamma,\delta)[\lambda(\alpha,\beta)\bar{\lambda}(\gamma,\delta)+\bar{\lambda}(\alpha,\beta)\lambda(\gamma,\delta)]\end{aligned} \tag{3.3}$$

or in tensor notation

$$\mathscr{V}=\underline{F}_1\cdot\underline{\Lambda}+\underline{\bar{F}}_1\cdot\underline{\bar{\Lambda}}+\tfrac{1}{2}\underline{\Lambda}\cdot\underline{F}_2\cdot\underline{\Lambda}-\underline{\Lambda}\cdot\underline{F}_2\cdot\underline{\bar{V}} , \tag{3.4}$$

where · signifies a contraction. The tensors $\underline{F}_1$ and $\underline{\bar{F}}_1$ can be decomposed into bond-stretching, axial-stretching, and bond-bending tensors, such as $\underline{F}_S$, $\underline{F}_A$, and $\underline{F}_B$; whereas, $\underline{F}_2$ becomes $\underline{F}_{SS}$, $\underline{F}_{BB}$, $\underline{F}_{SB}$, etc.

The various coupling constants of the Keating-Fuller expansion can be identified by inspection of the various configurations of interacting NN bonds in the complex. With the use of the set of 36 bond-deformation parameters, there are 36 first-order coupling constants and 1296 second-order coupling constants per central atom. These coupling constants can be subdivided as follows:

First order	Second order
6 bond stretching	36 bond stretching
6 axial stretching	36 axial stretching
24 bond bending	572 bond bending
	72 bond stretching with axial stretching
	288 bond stretching with bond bending
	288 axial stretching with bond bending

$\underline{F}_S$ is a symmetric, second-rank tensor containing two types of first-order bond-stretching constants. Since all six bonds are equivalent, the coefficients along the major diagonal, which describe the tensions associated with simple bond stretching, are equal so that a single coupling constant $f_S = f_{\alpha\alpha}$ can be defined. Similarly, the axial-stretching coefficients $f_{\alpha\bar{\alpha}}$ are all equal so that we can define $f_A \equiv f_{\alpha\bar{\alpha}}$.

$\underline{F}_B$ is a symmetric second-rank tensor containing the first-order bond angle bending coefficients, $f_{\alpha\beta}$ $(\alpha \neq \beta)$. Twenty-four of the off-diagonal constants associated with the deformation of the NN bond angles are equal, $f_{\alpha\beta} = f_B$, and the 12 remaining elements are 0.

Constraints are imposed on the first-order coupling constants by the condition that the energy $E(r',\theta')$ per unit cell have a minimum at the equilibrium values of the coordinates: $r' = r$, $\theta' = \theta$, which implies $\lambda = 0$. The total energy E per unit cell is given by

$$E(r',\theta') = -\alpha_M (Ze)^2/r' + \mathscr{V}_0 + \mathscr{V}(\lambda) , \tag{3.5}$$

where α_M is the Madelung constant, 1.747 558, Z is the magnitude of ionic charge in units of the charge e, and $\lambda = \lambda(r',\theta')$ according to Eq. (2.1). The equilibrium conditions are

$$(2f_S - f_A)/a + \tfrac{2}{3}\alpha_M f_o Z^2 = 0 , \tag{3.6a}$$

$$f_B = 0 , \tag{3.6b}$$

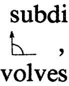
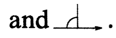
where

$$f_o = e^2/2\Omega_c . \tag{3.7}$$

It can also be shown that within the BDM formulation the force on any ion is unaffected by a uniform translation of the lattice.

$\underline{F}_{SS}$, $\underline{F}_{BB}$, etc., are six-dimensional, fourth-rank tensors containing the second-order coupling constants. A notation for the second-order interactions, the designation of the coupling constants, and their multiplicities are summarized in Table I. The multiplicity of a coupling constant is the number of times it is counted in Eq. (3.1).

The three types of bond deformations can be represented by the following symbols: bond stretching, ↑; axial stretching, ↕ ; bond bending, ⊾. Each of the interactions involving simple bond stretching (↑); regardless of the number of atoms involved, may be presumed to be of a central-force type. Thus the coupling constant $f_{SS}^{(1b)}$ while coupling the displacements of three atoms describes a central force interaction. However, as stated in Ref. 1, all three-body and higher-order interactions will be included under the category of NCF interactions, and CF interactions will be restricted to pairwise interactions. Axial-stretching interactions (↕) and bond-bending interactions (⊾ may contain both CF (bond-stretching) and NCF (angular deformation) components.

Second-order interactions are indicated by combining pairs of these symbols. Thus (↑⊾) indicates coupling of bond-stretching and bond-bending deformations. The interaction indicated by (↑⊾) can be subdivided into three geometrically distinct interactions:  ,  , and . The first of these interactions involves coupling of a change in bond angle with the changes in length of one of the bonds which form the bond angle. The second involves a bond which is normal to the plane of the bond angle. The third involves a bond which is coplanar with the bond angle but oppositely oriented with respect to one of the bonds which form the angle. Superscripts are used on the coupling constants to distinguish between geometrically different interactions of the same general type.

The multiplicities are listed in the fourth column of Table I. To obtain the multiplicity for an interaction a convenient scheme for counting is the following: set $\alpha = 1$; set $\beta = 1$ if $\alpha = \beta$, otherwise, $\beta = 2$; allow γ and δ to run over those indices which yield geometrically equivalent orientations with bonds α and β. This number of equivalent orientations is multiplied by 1 if $\beta = \alpha, \bar{\alpha}$ or by 4 if $\alpha \perp \beta$. The resulting product is multiplied by 2 if the deformations (α,β) and (γ,δ) are not similar. The product is multiplied by 6 to obtain the final result.

Musgrave and Pople[21] gave an alternative phenomenological description of the covalent interactions in the diamond structure. They termed their description the "valence force-field model" (VFFM). The expansion variables for their model are the bond lengths and bond angles. The VFFM can be used, also, as an alternate description of the short-range interactions in ionic compounds, and it is evident from Eq. (2.1) that there is a simple transformation between these two descriptions.

IV. NNN BOND-STRETCHING INTERACTIONS

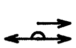
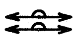
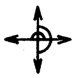
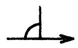
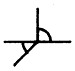
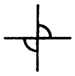
We first split the strain energy $\mathscr{V}$ into an NN part $\mathscr{V}_{\text{NN}}$ and an NNN part,

$$\mathscr{V}_{\text{NNN}} = g_S(\kappa)\lambda'(\epsilon,\epsilon;\kappa) + \tfrac{1}{2}g_{SS}^{(0)}(\kappa)[\lambda'(\epsilon,\epsilon;\kappa)]^2 + \tfrac{1}{2}g_{SS}^{(1t)}(\kappa)\lambda'(\epsilon,\epsilon;\kappa)\lambda'(\zeta,\zeta;\kappa) , \quad \kappa = A,B, \; t = a,b . \tag{4.1}$$

The indices ϵ and ζ, which run over the integers from 1 to 12, label the NNN bonds. These bonds are assigned as shown in Fig. 1(b). We have not followed the customary assignment in which each of the 12 NNN bonds has a terminus at the central atom; rather, we have selected the 12 NNN bonds which connect the 12 pairs of NNN atoms formed by the six atoms that are nearest neighbors to the central atom. It is obvious that in forming quantities such as the lattice energy the two methods of assigning NNN bonds lead to identical results.

The NNN bond-stretching parameters and coupling constants are the effective unit-cell quantities and, as in

TABLE I. Second-Order Interactions

Interactions	Coupling constants	Multiplicity	Interactions	Coupling constants	Multiplicity
1. Bond stretching			4. Bond stretching with axial stretching		
	$f_{SS}^{(0)}$	6			
	$f_{SS}^{(1a)}$	24		$f_{SA}^{(0)}$	24
	$f_{SS}^{(1b)}$	6		$f_{SA}^{(1)}$	48
2. Axial stretching			5. Bonding-stretching with bond bending		
	$f_{AA}^{(0)}$	12			
	$f_{AA}^{(1)}$	24		$f_{SB}^{(0)}$	96
				$f_{SB}^{(1a)}$	96
3. Bonding-bending					
	$f_{BB}^{(0)}$	48		$f_{SB}^{(1b)}$	96
	$f_{BB}^{(1a)}$	192			
			6. Axial stretching with bond bending		
	$f_{BB}^{(1b)}$	96			
	$f_{BB}^{(2a)}$	192		$f_{AB}^{(0)}$	192
	$f_{BB}^{(2b)}$	48		$f_{AB}^{(1)}$	96

Eqs. (2.19a) and (2.19b) and (3.2a)–(3.2d), have symmetric and asymmetric parts. However, for simplicity the asymmetric part of each quantity will be ignored here. An NNN bond-stretching deformation $\lambda'(\epsilon,\epsilon;\kappa)$ for the basis κ can be considered to be shared equally between two unit cells, as is the case for the NNN displacements in the rocksalt structure, so that each $\lambda'(\epsilon,\epsilon;\kappa)$ has an associated weight of $\frac{1}{2}$. These weights are subsumed into the effective unit-cell coupling constants in passing to the unit-cell formulation in Eq. (4.1); thus

$$g_S=\tfrac{1}{2}\sum_{\kappa} g_S(\kappa)\ , \tag{4.2a}$$

$$g_{SS}^{(0)}=\tfrac{1}{4}\sum_{\kappa} g_{SS}^{(0)}(\kappa)\ , \tag{4.2b}$$

$$g_{SS}^{(1t)}=\tfrac{1}{4}\sum_{\kappa} g_{SS}^{(1t)}(\kappa)\ . \tag{4.2c}$$

For the case of $g_{SS}^{(1t)}$, there are two distinguishable bond-stretching interactions which are symbolized in Eq. (4.1) and (4.2c) by $t=a$ or b. These two interactions are included to illustrate how NNN bond-stretching interactions other than the one characterized by $g_{SS}^{(0)}$ may enter the problem. Other couplings of NNN bond stretching in the complex may be possible but will not be considered here.

First, the coupling constant $g_{SS}^{(1a)}$ measures the magnitude of the interaction between two adjacent bonds lying in orthogonal planes. These bonds intersect at a 60° angle. There are 24 of these interactions implicit in Eq. (4.1), which can be readily ascertained from the 24 90° dihedral angles formed by these intersecting planes. The dihedral angles in each of the octants are counted separately.

Second, the coupling constant $g_{SS}^{(1b)}$ measures the interaction between the adjacent coplanar NNN bonds. These bonds intersect at a 90° angle. There are 12 of these interactions: four such interactions in each of the three orthogonal planes.

The reduction of Eq. (4.1) to the NN interactions described in Sec. III is carried out by substituting Eq. (2.10) into Eq. (4.1). Before doing this, it is desirable to convert Eq. (4.1) to the atom-pair notation which was used in the previous section. For example, using the NNN bond $\epsilon=3$,

$$\begin{aligned}&\lambda'(3,3)\ \text{(bond notation)}\\ &\rightarrow \tfrac{1}{2}[\lambda'(2,2;1)+\lambda'(1,1;2)]\ \text{(atom-pair notation)}\\ &\rightarrow \lambda(2,2)+\lambda(1,1)-\lambda(1,2)-\lambda(2,1)\ \text{(NN notation)}\ . \qquad (4.3)\end{aligned}$$

The NNN bond-deformation parameters in atom-pair notation, given in the first line, were transformed to NN bond-deformation parameters in the second line by means of Eq. (2.10). For the first-order interaction with the coupling constant g_S the 12 NNN terms go over to 24 NN bond-stretching terms and 24 bond-bending terms. The transformations of the second-order terms in Eq. (4.1) are summarized in Table II. In making these transformations for the second-order terms the cross products $\lambda'(\alpha,\alpha;\beta)\lambda'(\beta,\beta;\alpha)$ are not distinguished from the products $[\lambda'(\alpha,\alpha;\beta)]^2$ and $[\lambda'(\beta,\beta;\alpha)]^2$ and are not counted. This implies that the number of terms increases by a factor of 2 rather than a factor of 4 in going from the NNN bond notation to the NNN atom-pair notation.

A NN coupling constant f can be written in the general form

$$f=\hat{f}+Cg\ , \tag{4.4}$$

where $\hat{f}$ is a remaining NN term which measures the effect of the NN deformation at the central atom, and C is a numerical constant. Using the transformations detailed in Table II, Eq. (4.4) can be treated explicitly for each of the NN coupling constants:

$$f_S=\hat{f}_S+4g_S\ , \tag{4.5a}$$

$$f_B=\hat{f}_B-g_S\ , \tag{4.5b}$$

$$f_{SS}^{(0)}=\hat{f}\,_{SS}^{(0)}+4g_{SS}^{(0)}+8g_{SS}^{(1a)}+4g_{SS}^{(1b)}\ , \tag{4.5c}$$

$$f_{SS}^{(1a)}=\hat{f}\,_{SS}^{(1a)}+g_{SS}^{(0)}+6g_{SS}^{(1a)}+2g_{SS}^{(1b)}\ , \tag{4.5d}$$

$$f_{SS}^{(1b)}=\hat{f}\,_{SS}^{(1b)}+4g_{SS}^{(1b)}\ , \tag{4.5e}$$

$$f_{BB}^{(0)}=\hat{f}\,_{BB}^{(0)}+g_{SS}^{(0)}\ , \tag{4.5f}$$

$$f_{BB}^{(1a)}=\hat{f}\,_{BB}^{(1a)}+g_{SS}^{(1a)}\ , \tag{4.5g}$$

$$f_{BB}^{(1b)}=\hat{f}\,_{BB}^{(1b)}+g_{SS}^{(1b)}\ , \tag{4.5h}$$

$$f_{SB}^{(0)}=\hat{f}\,_{SB}^{(0)}-\tfrac{1}{2}g_{SS}^{(0)}-2g_{SS}^{(1a)}-g_{SS}^{(1b)}\ , \tag{4.5i}$$

$$f_{SB}^{(1a)}=\hat{f}\,_{SB}^{(1a)}-2g_{SS}^{(1a)}\ , \tag{4.5j}$$

$$f_{SB}^{(1b)}=\hat{f}\,_{SB}^{(1b)}-2g_{SS}^{(1b)}\ . \tag{4.5k}$$

The three NNN second-order bond-stretching interactions do not contribute to the NN coupling constants $f_{BB}^{(2a)}$ and $f_{BB}^{(2b)}$.

V. CENTRAL FORCES

Since pairwise CF interactions can be expected to contribute significantly to the coupling constants, these interactions are considered in this section. Thorough treatments of NN and NNN CF models for rocksalt-structure crystals have been given elsewhere.[19,20,22] The relevant portions of the CF theory will be summarized before deriving the CF contributions to the coupling constants.

Let $\Psi(r'(\epsilon,\zeta))$ be a CF potential between a pair of atoms ϵ and ζ, where $r'(\epsilon,\zeta)$ is the separation of the atoms such that

$$r(\epsilon,\zeta)=|\vec{r}(\epsilon)-\vec{r}(\zeta)|\ . \tag{5.1}$$

The first and second derivatives of $\Psi(r'(\epsilon\zeta))$ with respect to the separation $r'(\epsilon,\zeta)$ of the displaced atoms and evaluated at $r'(\epsilon,\zeta)=r(\epsilon,\zeta)$, are given, respectively, as

TABLE II. Transformation of NNN sums to NN sums.

Bonds		Atom pairs		Coupling constants	Bonds		Coupling constants
Term	No.	Term	No.		Term	No.	
$\lambda'_{\epsilon\epsilon}$	12	$\lambda'_{\alpha\alpha}(\beta)$	24	g_S	$\lambda_{\alpha\alpha}$	24	f_S
					$\lambda_{\alpha\beta}$	24	f_B
$(\lambda'_{\epsilon\epsilon})^2$	12	$[\lambda'_{\alpha\alpha}(\beta)]^2$	24	$g_{SS}^{(0)}$	$\lambda_{\alpha\alpha}^2$	24	$f_{SS}^{(0)}$
					$\lambda_{\alpha\alpha}\lambda_{\beta\beta}$	24	$f_{SS}^{(1a)}$
					$\lambda_{\alpha\beta}^2$	48	$f_{BB}^{(0)}$
					$\lambda_{\alpha\alpha}\lambda_{\alpha\beta}$	48	$f_{SB}^{(0)}$
$\lambda'_{\epsilon\epsilon}\lambda'_{\zeta\zeta}$	24	$\lambda'_{\alpha\alpha}(\gamma)\lambda'_{\beta\beta}(\gamma)$	48	$g_{SS}^{(1a)}$	$\lambda_{\alpha\alpha}^2$	48	$f_{SS}^{(0)}$
		$\angle\alpha\gamma\beta=60°$			$\lambda_{\alpha\alpha}\lambda_{\beta\beta}$	144	$f_{SS}^{(1a)}$
					$\lambda_{\alpha\beta}\lambda_{\beta\gamma}$	192	$f_{BB}^{(1a)}$
					$\lambda_{\alpha\alpha}\lambda_{\alpha\beta}$	192	$f_{SB}^{(0)}$
					$\lambda_{\alpha\alpha}\lambda_{\beta\gamma}$	192	$f_{SB}^{(1a)}$
$\lambda'_{\epsilon\epsilon}\lambda'_{\zeta\zeta}$	12	$\lambda'_{\alpha\alpha}(\gamma)\lambda'_{\beta\beta}(\gamma)$	24	$g_{SS}^{(1b)}$	$\lambda_{\alpha\alpha}^2$	24	$f_{SS}^{(0)}$
		$\angle\alpha\gamma\beta=90°$			$\lambda_{\alpha\alpha}\lambda_{\gamma\gamma}$	48	$f_{SS}^{(1a)}$
					$\lambda_{\alpha\alpha}\lambda_{\beta\beta}$	24	$f_{SS}^{(1b)}$
					$\lambda_{\alpha\gamma}\lambda_{\gamma\beta}$	96	$f_{BB}^{(1b)}$
					$\lambda_{\alpha\alpha}\lambda_{\alpha\gamma}$	96	$f_{SB}^{(0)}$
					$\lambda_{\alpha\alpha}\lambda_{\beta\gamma}$	96	$f_{SB}^{(1b)}$

$$\Psi_i(r(\epsilon,\zeta)) = \left.\frac{\partial\Psi(r'(\epsilon,\zeta))}{\partial x_i'}\right|_0 = \frac{x_i}{r}\Psi'(r)\,, \tag{5.2a}$$

$$\Psi_{ij}(r(\epsilon,\zeta)) = \left.\frac{\partial^2\Psi(r'(\epsilon,\zeta))}{\partial x_i'\,\partial x_j'}\right|_0 = \frac{x_i x_j}{r^2}\left[\Psi''(r) - \frac{1}{r}\Psi'(r)\right] + \delta_{ij}\frac{1}{r}\Psi'(r)\,, \tag{5.2b}$$

where a prime on $\Psi(r)$ denotes differentiation with respect to the argument r. In parametrizing the derivatives $\Psi'(r)$ and $\Psi''(r)$ we follow the notation of Hardy and Karo,[23] who used the letters A and B to designate the second and first derivatives, respectively; a prime ($'$) to designate NN interactions; and a double prime ($''$) to designate NNN interactions. Thus the derivatives $\Psi'(r)$ and $\Psi''(r)$ may be parametrized as follows.

(1) NN interactions,

$$f_o A' = \Psi''_{+-}(r)\,, \tag{5.3a}$$

$$f_o B' = (1/r)\Psi''_{+-}(r)\,, \tag{5.3b}$$

(2) NNN interactions,

$$f_o A''(--) = \Psi''_{--}(r)\,, \tag{5.4a}$$

$$f_o B''(--) = (1/r)\Psi'_{--}(r)\,, \tag{5.4b}$$

$$f_o A''(++) = \Psi''_{++}(r)\,, \tag{5.4c}$$

$$f_o B''(++) = (1/r)\Psi'_{++}(r)\,, \tag{5.4d}$$

and

$$A'' = A''(++) + A''(--)\,, \tag{5.5a}$$

$$B'' = B''(++) + B''(--)\,, \tag{5.5b}$$

where f_o is given by Eq. (3.7). We also define the asymmetric quantities

$$\bar{A}'' = A''(++) - A''(--)\,, \tag{5.6a}$$

$$\bar{B}'' = B''(++) - B''(--)\,, \tag{5.6b}$$

which can be used to parametrize some of the CF terms in lattice-dynamical expressions.

The derivatives of a central-force potential are expected to be associated with coupling constants which are coefficients for the stretching of single NN and NNN bonds. With the use of the results of Sec. IV the coupling constants are split into NN and NNN parts. These parts are associated with the appropriate derivatives of the short-range potential Φ_{SR}.

Considering first the NN terms, the BDM expansion of the NN part, Φ_{NN}, of Φ_{SR} can be differentiated with respect to the components of $x_i'(\epsilon,\nu)$, according to Eqs. (A7a) and (A7b). The derivatives of Φ_{NN} are

$$\Phi_{\mathrm{NN},i}(\epsilon,\nu) = (\epsilon\nu,i)[2\hat{f}_S(\nu) - \hat{f}_A(\nu)]\,, \tag{5.7a}$$

$$\Phi_{\mathrm{NN},ij}(\epsilon,\nu) = 2\hat{f}_S(\nu)\delta_{ij}/a + [4\hat{f}^{(0)}_{SS}(\nu) + f^{(0)}_{AA}(\nu) - 4f^{(0)}_{SA}(\nu)](\epsilon\nu;i)^2\delta_{ij} + \tfrac{1}{2}[\hat{f}^{(0)}_{BB}(\nu) - \hat{f}^{(1b)}_{BB}(\nu)][1 - (\epsilon\nu,i)^2]\delta_{ij}\,, \tag{5.7b}$$

where the summation formulas, Eqs. (A4a)–(A4c) and (A6), have been used in obtaining Eq. (5.7b). Requiring that $\Phi_{\mathrm{NN},i}(\epsilon,\nu)$ and $\Phi_{\mathrm{NN},ij}(\epsilon,\nu;\epsilon,\nu)$ contain only coupling constants associated with NN pairwise interactions yields the conditions

$$\hat{f}_A(\nu) = 0\,, \tag{5.8a}$$

$$f^{(0)}_{AA}(\nu) - 4f^{(0)}_{SA}(\nu) = 0\,, \tag{5.8b}$$

$$\hat{f}^{(0)}_{BB}(\nu) - \hat{f}^{(1b)}_{BB}(\nu) = 0\,. \tag{5.8c}$$

Equation (5.7b) becomes

$$\Phi_{\mathrm{NN},ij}(\epsilon,\nu) = 2\hat{f}_S(\nu)\delta_{ij}/a + 4(\epsilon\nu,i)^2\hat{f}^{(0)}_{SS}(\nu)\delta_{ij}\,. \tag{5.9}$$

The matrix $\underline{\Phi}_{\mathrm{NN}}(\epsilon,\mu;\epsilon,\mu)$ can be identified with the CF matrix $\underline{\Phi}(0,0,0;0,0,0)$ for the rocksalt structure—see Eq. (6.3.3b) of Ref. 20. The first term on the right-hand side of Eq. (5.9) applies to both longitudinal and transverse displacements of the atoms with respect to the bond direction, whereas the second term only applies to longitudinal displacements. Since Φ_{NN} is assumed here to consist of CF interactions, Eqs. (2.1.37), (2.1.38), and (2.1.39) of Ref. 20 can be used to write the derivatives of Φ_{NN} as

$$\Phi_{\mathrm{NN},i}(\epsilon,\nu) = \frac{1}{2}\left.\frac{\partial\Psi_{+-}(r')}{\partial x_i'}\right|_0 = \tfrac{1}{2}(\epsilon\nu,i)af_oB'(\nu)\,, \tag{5.10a}$$

$$\Phi_{\mathrm{NN},ij}(\epsilon,\nu) = \frac{1}{2}\left.\frac{\partial^2\Psi_{+-}(r')}{\partial x_i'\,\partial x_j'}\right|_0 = \tfrac{1}{2}\{(\epsilon\nu,i)(\epsilon\nu,i)f_o[A'(\nu) - B'(\nu)] + \delta_{ij}f_oB'(\nu)\}\,, \tag{5.10b}$$

where the factor $\frac{1}{2}$, rather than $\frac{1}{4}$, is required in Eq. (5.10b) since the order of differentiation is immaterial.

Identifying coefficients in Eqs. (5.7a) and (5.10a), we obtain

$$4\hat{f}_S(\nu) = af_oB'(\nu)\,. \tag{5.11}$$

Since B' does not depend on the choice of bond origin, that is,

$$B'(+) = B'(-) = B' \tag{5.12}$$

it follows that

$$\hat{f}_S(+)=\hat{f}_S(-) , \tag{5.13}$$

and with the use of Eq. (3.2a), it follows that

$$2\hat{f}_S=af_oB' . \tag{5.14}$$

By the identification of terms in Eqs. (5.9) and (5.10b), the second-order coupling constant $\hat{f}_{SS}^{(0)}(v)$ can be expressed in terms of the derivatives A' and B':

$$8\hat{f}_{SS}^{(0)}(v)=f_o[A'(v)-B'(v)] . \tag{5.15}$$

Since $A'(v)$ and $B'(v)$ are independent of the basis of the central atom, it follows that $\hat{f}_{SS}^{(0)}(v)$ is independent of v and that

$$4\hat{f}_{SS}^{(0)}=f_o[A'-B'] \tag{5.16}$$

for the unit-cell coupling constant.

Taking Eq. (4.1) to represent the contribution of NNN bonds to Φ_{SR}, we proceed as for the NN part to find the CF terms by taking derivatives of Φ_{NNN}. From $\Phi_{NNN,i}(\epsilon,v)$ we obtain

$$2\sqrt{2}g_S(v)=\Psi'_{vv}(r)=a\sqrt{2}f_oB''(v) , \tag{5.17}$$

where v identifies the sublattice. The unit-cell coupling constants can be obtained by summing over v, thus

$$4g_S=af_oB'' . \tag{5.18}$$

From $\Phi_{NNN,ij}(\epsilon,v;\epsilon,v)$ we obtain

$$4g_{SS}^{(0)}(v)=f_o[A''(v)-B''(v)] \tag{5.19}$$

and summing over v,

$$16g_{SS}^{(0)}=f_o[A''-B''] . \tag{5.20}$$

Equations (5.14), (5.16), (5.18), and (5.20) can be substituted into Eqs. (4.5a) and (4.5c) to obtain

$$2f_S=af_o[B'+2B''] , \tag{5.21a}$$

$$4f_{SS}^{(0)}=f_o[A'+A''-B'-B'']+16[2g_{SS}^{(1a)}+g_{SS}^{(1b)}] , \tag{5.21b}$$

where the first term on the right-hand side of Eq. (5.21b) represents the pairwise central forces. Similarly Eq. (5.20) can be used to incorporate the derivatives of Ψ_{NNN} into the expressions for $f_{SS}^{(1a)}$, $f_{BB}^{(0)}$, and $f_{SB}^{(0)}$ by using Eqs. (4.5d), (4.5f), and (4.5i), respectively. If we require that $f_{SS}^{(0)}$ arises only from pairwise CF interactions, then it is necessary to impose the condition that

$$2g_{SS}^{(1a)}+g_{SS}^{(1b)}=0 \tag{5.22}$$

The three-body coupled bond-stretching interaction described by $f_{SS}^{(1b)}(v)$ may be similar to the first-order axial-stretching interaction described by $f_A(v)$, if this latter interaction does not contain a NCF component. Since by Eq. (5.8a) $f_A(v)$ vanishes, it may be expected that $f_{SS}^{(1b)}(v)$ vanishes as well.

VI. LATTICE DYNAMICS

The natural variables for lattice dynamics are the atomic displacements, $\{\vec{u}(\alpha)\}$, in which the potential is usually expanded to second order for the harmonic approximation.[20] The coefficients for the expansion of the potential energy of the lattice in these variables are the atomic force constants. The lattice dynamics of ionic crystals, particularly of the NaCl-type, have been discussed by a number of authors; for reviews of this subject see Born and Huang,[19] Maradudin *et al.*,[20] and Hardy and Karo,[23] as well as Cochran[24,25] and Basu *et al.*[26] Hardy and Karo, Cochran, Basu *et al.* included discussions of noncentral forces in their reviews. The ground work will be established here for obtaining the short-range force constants of the dynamical matrix from the BDM.

An expansion of the potential energy in the bond-deformation parameters mixes several orders of atomic displacements so that the BDM, as presented in Sec. III, cannot be used easily to describe the dynamics of a crystal. However, the set $\{\mu\}$ of new bond-deformation parameters can be easily related to the atomic displacements. We will examine first the relationship of the μ parameters to the atomic displacements and then will give the transformation of the old set of coupling constants $\{f\}$ to a new set $\{h\}$, the elements of which are the coefficients for the expansion of the strain energy in the μ parameters. The harmonic short-range potential can be extracted easily by neglecting terms which are higher than second order in the atomic displacements. The coefficients of the dynamical matrix of short-range force constants will not be derived here.

The new bond-deformation parameters given by the transformation defined by Eqs. (2.11) and (2.12) are readily expressed in terms of the relative atomic displacements, $\vec{u}(\alpha,v)$, by using Eqs. (2.1) and (2.3). Thus

$$\mu(\alpha,\beta;v)=[\vec{u}(\alpha,v)+\vec{u}(\bar{\alpha},v)]\cdot[\vec{u}(\beta,v)+\vec{u}(\bar{\beta},v)]/4a , \tag{6.1a}$$

$$\begin{aligned}\mu(\bar{\alpha},\beta;v)=&-\{\vec{r}(\alpha,v)\cdot[\vec{u}(\beta,v)-\vec{u}(\bar{\beta},v)]+\vec{r}(\beta,v)\cdot[\vec{u}(\alpha,v)-\vec{u}(\bar{\alpha},v)]\}/2a\\&-[\vec{u}(\alpha,v)-\vec{u}(\bar{\alpha},v)]\cdot[\vec{u}(\beta,v)-\vec{u}(\bar{\beta},v)]/4a ,\end{aligned} \tag{6.1b}$$

$$\mu(\alpha,\bar{\beta};v)=-i[\vec{u}(\alpha,v)+\vec{u}(\bar{\alpha},v)]\cdot[2\vec{r}(\beta,v)+\vec{u}(\beta,v)-\vec{u}(\beta,v)]/4a , \tag{6.1c}$$

$$\mu(\bar{\alpha},\beta;v)=-i[\vec{u}(\beta,v)+\vec{u}(\beta,v)]\cdot[2\vec{r}(\alpha,v)+\vec{u}(\alpha,v)-\vec{u}(\bar{\alpha},v)]/4a . \tag{6.1d}$$

The atomic displacements $\{\vec{u}(\alpha)\}$ can be assumed to have plane-wave solutions.

The strain energy can be expanded in the μ's in a manner analogous to Eq. (3.1):

$$\mathscr{V}=h(\alpha,\beta;v)w'_{\alpha\beta}\mu(\alpha,\beta;v)+\tfrac{1}{2}h(\alpha,\beta;\gamma,\delta;v)w'_{\alpha\beta}w'_{\gamma\delta}\mu(\alpha,\beta;v)\mu(\gamma,\delta;v),\quad \alpha,\beta,\ldots=1-6 . \tag{6.2}$$

The weights $w'_{\alpha\beta}$ are analogous to the weights introduced in Sec. III. The first-order constants $h(\alpha,\beta;\nu)$ can be obtained from the first-order f-type constants by the transformation

$$h(\alpha,\beta;\nu)w'_{\alpha\beta}=b_{\alpha\epsilon}b_{\beta\zeta}f(\epsilon,\zeta;\nu)w_{\epsilon\zeta}\ , \tag{6.3}$$

and the second-order constants $h(\alpha,\beta;\gamma,\delta;\nu)$, by

$$\begin{aligned} h(\alpha,\beta;\gamma,\delta;\nu)w'_{\alpha\beta}w'_{\gamma\delta}\\ =b_{\alpha\epsilon}b_{\beta\zeta}b_{\gamma\eta}b_{\delta\theta}f(\epsilon,\zeta;\eta,\theta;\nu)\cdot w_{\epsilon\zeta}w_{\eta\theta}\ , \end{aligned} \tag{6.4}$$

where

$$\underline{b}=\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 1\\ 0 & 1 & 0 & 0 & 1 & 0\\ 0 & 0 & 1 & 1 & 0 & 0\\ 0 & 0 & i & -i & 0 & 0\\ 0 & i & 0 & 0 & -i & 0\\ i & 0 & 0 & 0 & 0 & -i \end{bmatrix}\ . \tag{6.5}$$

According to Eqs. (3.1a)–(3.1d) and (6.5), the unit-cell h-coupling constants and f-coupling constants are related by

$$h(\alpha,\beta)=b_{\alpha\epsilon}b_{\beta\zeta}f(\epsilon,\zeta) \tag{6.6}$$

for the first-order constants, and

$$h(\alpha,\beta;\gamma,\delta)=b_{\alpha\epsilon}b_{\beta\zeta}b_{\gamma\eta}b_{\delta\theta}f(\epsilon,\zeta;\eta,\theta) \tag{6.7}$$

for the second-order constants. Similar transformations apply to the asymmetric unit-cell coupling constants. The nonzero symmetric unit-cell coupling constants, $h(\alpha,\beta)$ and $h(\alpha,\beta;\gamma,\delta)$, are given in Table III. In Table III, we use the convention that $\alpha,\beta,\ldots=1$–3 and $\bar{\alpha},\bar{\beta},\ldots=4$–$6$. We note from Table III that if the f-type constants are real, the h-type constants also are real.

Using the first-NN pairwise interaction condition, Eq. (5.8a),

$$h(\alpha,\alpha)=-h(\bar{\alpha},\bar{\alpha})=2\bar{f}_S\ , \tag{6.8a}$$

$$\bar{h}(\alpha,\alpha)=2\bar{f}_S\ , \tag{6.8b}$$

where f_S is given by Eq. (5.21b) and

$$\bar{f}_S=af_o\bar{B}''\ . \tag{6.9}$$

The second-NN pairwise interaction condition, Eq. (5.8b), can be used to simplify the expressions for $h(\alpha,\alpha;\alpha,\alpha)$ and $h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})$; thus,

$$h(\alpha,\alpha;\alpha,\alpha)=2f_{SS}^{(0)}+2f_{SS}^{(1b)}+8f_{AA}^{(0)}\ , \tag{6.10a}$$

$$h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})=2f_{SS}^{(0)}+2f_{SS}^{(1b)}\ . \tag{6.10b}$$

Since NN CF interactions are symmetric with respect to the basis, it follows that terms for these interactions will appear in symmetric coupling constants such as $h(\alpha,\alpha;\alpha,\alpha)$ and $h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})$ but will not appear in the asymmetric analogs of these constants. However, NNN CF terms are not generally symmetric with respect to the basis so that NNN CF terms can be expected to appear in both the symmetric and the asymmetric coupling constants.

It is apparent from Eqs. (6.1a)–(6.1c) that Eq. (6.2) is quartic in the atomic displacements. To obtain the harmonic potential it is necessary to extract the quadratic portion from Eq. (6.2). The first-order terms in the harmonic potential go over the equilibrium condition Eq. (3.6a) when the electrostatic part of the potential is included. The second-order terms arise from terms in Eq. (6.2) which are first-order in $\mu(\alpha,\beta;\nu)$ [see Eq. (6.1a)] and second-order in $\mu(\bar{\alpha},\bar{\beta};\nu)$ [see Eq. (6.1b)]. It can be shown that second-order terms in $\mu(\alpha,\bar{\beta};\nu)$ [see Eq. (6.1c)] do not contribute because their sums vanish due to the condition

$$\vec{r}(\alpha,\nu)+\vec{r}(\bar{\alpha},\nu)=0\ . \tag{6.11}$$

Cross products of $\mu(\bar{\alpha},\bar{\beta};\nu)$ and $\mu(\alpha,\bar{\beta};\nu)$ do not appear because the associated coupling constants are null. We see from Table III that there are three types of second-order μ-coupling constants which appear in the second-order part, $\mathscr{V}_2$, of the harmonic potential $\mathscr{V}_h$: $h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})$, $h(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta})$, and $h(\bar{\alpha},\beta;\bar{\alpha},\beta)$. After some manipulation and explicitly noting the sum over the basis index ν, we obtain

$$\begin{aligned}\mathscr{V}_2=&(f_S/a)\{[u(\alpha,\nu)]^2+[u(\bar{\alpha},\nu)]^2\}+\tfrac{1}{2}h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha};\nu)[u_L(\alpha,\nu)+u_L(\bar{\alpha},\nu)]^2\\ &+\tfrac{1}{2}h(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta};\nu)[u_L(\alpha,\nu)+u_L(\bar{\alpha},\nu)][u_L(\beta,\nu)+u_L(\bar{\beta},\nu)]\\ &+\tfrac{1}{128}h(\bar{\alpha},\bar{\beta};\bar{\alpha},\bar{\beta};\nu)[u_T(\alpha,\nu;\beta)+u_T(\alpha,\nu;\beta)+u_T(\beta,\nu;\alpha)+u_T(\bar{\beta},\nu;\bar{\alpha})]^2\\ &-\tfrac{1}{8}h(\alpha,\bar{\alpha};\alpha,\bar{\alpha};\nu)[u_L(\alpha,\nu)-u_L(\bar{\alpha},\nu)]^2-\tfrac{1}{128}h(\alpha,\bar{\beta};\alpha,\bar{\beta};\nu)[u_T(\alpha,\nu;\beta)-u_T(\bar{\alpha},\nu;\bar{\beta})]^2\\ &-\tfrac{1}{128}h(\bar{\alpha},\beta;\bar{\alpha},\beta;\nu)[u_T(\beta,\nu;\alpha)-u_T(\bar{\beta},\nu;\bar{\alpha})]^2\\ &-\tfrac{1}{128}h(\alpha,\bar{\beta};\bar{\beta},\gamma;\nu)[u_T(\alpha,\nu;\beta)-u_T(\bar{\alpha},\nu;\bar{\beta})][u_T(\gamma,\nu;\beta)-u_T(\bar{\gamma},\nu;\beta)]\ ,\end{aligned} \tag{6.12}$$

where

$$u(\alpha,\nu)=|\vec{u}(\alpha,\nu)|\ , \tag{6.13a}$$

$$u_L(\alpha,\nu)=\vec{r}(\alpha,\nu)\cdot\vec{u}(\alpha,\nu)/a\ , \tag{6.13b}$$

$$u_T(\alpha,\nu;\beta)=\vec{r}(\beta,\nu)\cdot\vec{u}(\alpha,\nu)/a,\ \ \alpha\perp\beta\ . \tag{6.13c}$$

Equation (6.13a) defines the magnitude of the displacement, $\vec{u}(\alpha,\mu)$; Equation (6.13b), the longitudinal component of the displacement; and Eq. (6.13c), a transverse component which is parallel to the bond direction $\vec{r}(\beta,\mu)$. Note that the use of Eq. (6.11) in obtaining Eq. (6.12) requires changes in sign before displacement terms containing $\bar{\alpha}$ or $\bar{\beta}$. Equation (6.12) can be used to derive the short-range components of the dynamical matrix.

TABLE III. h-type coupling constants and equivalent combinations of f-type coupling constants. Indices $\alpha,\beta,\ldots=1-3$; $\bar{\alpha},\bar{\beta},\ldots=4-6$.

h type Term	No.	Equivalent f-type expression First-order coupling constants
$h(\alpha,\alpha)$	3	$2f_S+2f_A$
$h(\bar{\alpha},\bar{\alpha})$	3	$-2f_S+2f_A$
Term	No.	Second-order coupling constants
$h(\alpha,\alpha;\alpha,\alpha)$	3	$2f_{SS}^{(0)}+2f_{SS}^{(1b)}+4f_{AA}^{(0)}+8f_{SA}^{(0)}$
$h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})$	3	$2f_{SS}^{(0)}+2f_{SS}^{(1b)}+4f_{AA}^{(0)}-8f_{SA}^{(0)}$
$h(\alpha,\bar{\alpha};\alpha,\bar{\alpha})$	12	$-2f_{SS}^{(0)}+2f_{SS}^{(1b)}$
$h(\alpha,\alpha;\bar{\alpha},\bar{\alpha})=h(\bar{\alpha},\bar{\alpha};\alpha,\alpha)$	6	$-2f_{SS}^{(0)}-2f_{SS}^{(1b)}+4f_{AA}^{(0)}$
$h(\alpha,\alpha;\beta,\beta)$	6	$4f_{SS}^{(1a)}+4f_{AA}^{(1)}+8f_{SA}^{(1)}$
$h(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta})$	6	$4f_{SS}^{(1a)}+4f_{AA}^{(1)}-8f_{SA}^{(1)}$
$h(\alpha,\alpha;\bar{\beta},\bar{\beta})=h(\bar{\alpha},\alpha;\beta,\beta)$	12	$-4f_{SS}^{(1a)}+4f_{AA}^{(1)}$
$h(\alpha,\beta;\alpha,\beta)$	12	$4f_{BB}^{(0)}+8f_{BB}^{(1b)}+4f_{BB}^{(2b)}$
$h(\bar{\alpha},\bar{\beta};\bar{\alpha},\bar{\beta})$	12	$4f_{BB}^{(0)}-8f_{BB}^{(1b)}+4f_{BB}^{(2b)}$
$h(\alpha,\bar{\beta};\alpha,\bar{\beta})=h(\bar{\alpha},\beta;\bar{\alpha},\beta)$	24	$-4f_{BB}^{(0)}+4f_{BB}^{(1b)}$
$h(\alpha,\beta;\beta,\gamma)$	24	$8f_{BB}^{(1a)}+8f_{BB}^{(2a)}$
$h(\alpha,\bar{\beta};\bar{\beta},\gamma)$	24	$-8f_{BB}^{(1a)}+8f_{BB}^{(2a)}$
$h(\alpha,\alpha;\alpha,\beta)$	24	$4f_{SB}^{(0)}+4f_{SB}^{(1b)}+8f_{AB}^{(0)}$
$h(\alpha,\alpha;\beta,\gamma)$	12	$8f_{SB}^{(1a)}+8f_{AB}^{(1a)}$
$h(\bar{\alpha},\bar{\alpha};\alpha,\beta)$	24	$-4f_{SB}^{(0)}-4f_{SB}^{(1b)}+8f_{AB}^{(0)}$

In addition to the first-order parameter given by Eq. (6.8), the short-range harmonic potential is specified by six symmetric second-order unit-cell coupling constants:

$$h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha}),\ \ h(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta}),\ \ h(\bar{\alpha},\bar{\beta};\bar{\alpha},\bar{\beta})\ ,$$

$$h(\alpha,\bar{\alpha};\alpha,\bar{\alpha}),\ \ h(\alpha,\bar{\beta};\alpha,\bar{\beta}),\ \ h(\alpha,\bar{\beta};\bar{\beta},\gamma)\ ,$$

and by six asymmetric second-order unit-cell coupling constants

$$\bar{h}(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha}),\ \ \bar{h}(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta}),\ \ \bar{h}(\bar{\alpha},\bar{\beta};\bar{\alpha},\bar{\beta})\ ,$$

$$\bar{h}(\alpha,\bar{\alpha};\alpha,\bar{\alpha}),\ \ \bar{h}(\alpha,\bar{\beta};\alpha,\bar{\beta}),\ \ \bar{h}(\alpha,\bar{\beta};\bar{\beta},\gamma)\ .$$

The asymmetric coupling constants can be formed from the $\bar{f}$-coupling constants in a manner analogous to that for the symmetric constants by substituting the appropriate $\bar{f}$-coupling constants, as defined by Eq. (3.2d), into Eq. (6.7) or into the expressions for the corresponding symmetric coupling constants in Table III. In the special case where the NNN-CF and -NCF interactions are centered only on the anions (B-type atoms), the asymmetric coupling constants can be obtained from the symmetric coupling constants since

$$h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})=\hat{f}_{SS}^{(0)}-\bar{h}(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})\ , \tag{6.14a}$$

$$h(\alpha,\bar{\alpha};\alpha,\bar{\alpha})=-2\hat{f}_{SS}^{(0)}-\bar{h}(\alpha,\bar{\alpha};\alpha,\bar{\alpha})\ , \tag{6.14b}$$

$$h(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta})=-\bar{h}(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta})\ , \tag{6.14c}$$

$$h(\bar{\alpha},\bar{\beta};\bar{\alpha},\bar{\beta})=-\bar{h}(\bar{\alpha},\bar{\beta};\bar{\alpha},\bar{\beta})\ , \tag{6.14d}$$

$$h(\alpha,\bar{\beta};\alpha,\bar{\beta})=-\bar{h}(\alpha,\bar{\beta};\alpha\bar{\beta})\ , \tag{6.14e}$$

$$h(\alpha,\bar{\beta};\bar{\beta},\gamma)=-\bar{h}(\alpha,\bar{\beta};\bar{\beta},\gamma)\ . \tag{6.14f}$$

The term $\hat{f}_{SS}^{(0)}$ may be calculated [see Eq. (5.16)] from the derivatives A' and B' of the NN-CF potential.

VII. ELASTIC CONSTANTS AND EMPIRICAL FORCE CONSTANTS

Since the bond-deformation parameters are closely associated with the lattice strain η and the internal strain $\vec{w}$, according to Eq. (2.18) or according to Eq. (2.20a)–(2.20d) the BDM coupling constants can be easily related to the elastic constants and to the force constant for the homogeneous polarization of the lattice (internal strain). Proceeding in the manner of Brugger[27] we take derivatives of the potential energy Φ of the lattice with respect to the strains η and $\vec{w}$. The first derivative of Φ with respect to η is the tension, which must vanish; this condition is equivalent to Eqs. (3.6a) and (3.6b). With the use of Eq. (6.2) to express $\mathscr{V}$ in the μ parameters, the second-order derivatives of $\mathscr{V}$ can be taken with respect to the lattice strain components and then evaluated with the help of Eq. (A3b). For ionic crystals the long-range electrostatic contributions to the strain derivatives must be included. These were evaluated for the rocksalt lattice by Fuller and Naimon.[28]

The second-order Brugger elastic constants are defined, in tensor notation, as

$$C_{ij,hl}=\left.\frac{\partial^2 U}{\partial\eta_{ij}\partial\eta_{hl}}\right|_0 , \tag{7.1}$$

where $U=\mathscr{V}/\Omega_c$. These can be expressed in the matrix notation of Voigt[29] by using the following correspondence:

tensor	1,1	2,2	3,3	2,3;3,2	3,1;1,3	1,2;2,1
matrix	1	2	3	4	5	6

The elastic constants are

$$C_{11}=C_{22}=C_{33}$$
$$=[2h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})+C_{11}(\mathrm{ES})f_o Z^2]/a\ , \tag{7.2a}$$
$$C_{12}=C_{23}=C_{31}$$
$$=[2h(\bar{\alpha},\bar{\alpha};\bar{\beta},\bar{\beta})+C_{12}(\mathrm{ES})f_o Z^2]/a\ , \tag{7.2b}$$
$$C_{44}=C_{55}=C_{66}$$
$$=[2h(\bar{\alpha},\bar{\beta};\bar{\alpha},\bar{\beta})+C_{44}(\mathrm{ES})\mathrm{f}_o Z^2]/a\ , \tag{7.2c}$$

where ES represents electrostatic, and where $C_{11}(\mathrm{ES})=-6.277\,117$, $C_{12}(\mathrm{ES})=C_{44}(\mathrm{ES})=1.390\,994$, and

$$C_{11}(\mathrm{ES})+2C_{12}(\mathrm{ES})=-2\alpha_M\ . \tag{7.3}$$

Comparing Eq. (6.12) with Eqs. (7.2a)–(7.2c) it is evident that the elastic constants determine three symmetric second-order unit-cell h-coupling constants which are required for the dynamical matrix. Harmonic values[30] of the elastic constants, or to a good approximation, the liquid-helium temperature values of these parameters,[31] are the appropriate experimental quantities for use in evaluating the coupling constant considered here.

Using the expressions for $h(\bar{\alpha},\bar{\alpha};\bar{\alpha},\bar{\alpha})$, etc., in Table III and the results of Sec. V, we define the short-range CF coefficients

$$f_o C_{11}(\mathrm{CF})=4\hat{f}^{(0)}_{SS}+16g^{(0)}_{SS}$$
$$=f_o(A'+A''-B'-B'')\ , \tag{7.4a}$$
$$f_o C_{12}(\mathrm{CF})=8g^{(0)}_{SS}=\tfrac{1}{2}f_o(A''-B'')\ , \tag{7.4b}$$
$$C_{44}(\mathrm{CF})=C_{12}(\mathrm{CF})\ , \tag{7.4c}$$

and the short-range NCF coefficients

$$f_o C_{11}(\mathrm{NCF})=4\hat{f}^{(1b)}_{SS}+16g^{(1b)}_{SS}\ , \tag{7.5a}$$
$$f_o C_{12}(\mathrm{NCF})=8(\hat{f}^{(1a)}_{SS}+f^{(1)}_{AA}-2f^{(1)}_{SA}-g^{(1b)}_{SS})\ , \tag{7.5b}$$
$$f_o C_{44}(\mathrm{NCF})=-8(\hat{f}^{(0)}_{BB}-f^{(2b)}_{BB}+2g^{(1b)}_{SS})\ . \tag{7.5c}$$

The expressions for the NCF terms, Eqs. (7.5a)–(7.5c), were simplified here by assuming that $f^{(0)}_{SS}$ results only from CF interactions [see Eq. (5.22)] and by using Eqs. (5.8b) and (5.8c).

In the special case of CF conditions, where $C_{11}(\mathrm{NCF})$, $C_{12}(\mathrm{NCF})$, and $C_{44}(\mathrm{NCF})$ vanish, the Cauchy condition, $C_{12}=C_{44}$, is recovered. Empirically, however, these two elastic constants are not found to be equal so that a finite value for a so-called "Cauchy discrepancy,"

$$f_o B(\mathrm{NCF})=a(C_{44}-C_{12})\ , \tag{7.6}$$

generally is obtained. B(NCF) is defined according to the first equality in Eq. (7.15) of Hardy and Karo.[23] They make the further assumption, following Woods *et al.*,[32] that

$$f_o B(\mathrm{NCF})=\left[\frac{d^2\Phi_{\mathrm{NN}}(r)}{dr_\perp^2}\right]_{r=a}\ , \tag{7.7}$$

where $dr_\perp$ refers to a variation perpendicular to the bond. This further assumption applies if only the coupling constant $f^{(0)}_{BB}$ is significant, such as in the model proposed by Cunningham,[4] in which the inequality $C_{12}\neq C_{44}$ arises from an angle-bending interaction.

The force constant R for the uniform compression of the lattice is proportional to the bulk modulus $\mathscr{B}$ [see Eq. (9.29) of Ref. 19], where for a material with a cubic crystal structure

$$\mathscr{B}=(C_{11}+2C_{12})/3\ . \tag{7.8}$$

The force constant can be written as

$$R=6a\mathscr{B}=R(\mathrm{CF})+R(\mathrm{NCF}) \tag{7.9}$$

where

$$R(\mathrm{CF})=2f_0(A'+2A''-B'-2B''-2\alpha_M Z^2)\ , \tag{7.10a}$$
$$R(\mathrm{NCF})=8(4\hat{f}^{(1a)}_{SS}+\hat{f}^{(1b)}_{SS}+4f^{(1)}_{AA}-8f^{(1)}_{\mathrm{SA}})\ . \tag{7.10b}$$

The electrostatic term $\alpha_M Z^2$ in Eq. (7.10a) can be eliminated with the use of Eqs. (3.6a), (5.8a), and (5.21a). Equation (5.22) was used in obtaining Eq. (7.10b). Equation (7.10b) implies that there can be NCF contributions to the bulk modulus, which arise from coupled dilations and contractions of adjacent bonds. Since the derivatives, A'' and B'', of the NNN-CF potential are usually small relative to the derivatives A' and B', and since the potentials from which A' and B' are obtained often have two parameters to be determined empirically, a further practical assumption is

$$R(\mathrm{NCF})=0\ . \tag{7.11}$$

This assumption then allows A' and B' to be estimated from Eq. (7.9) and the equilibrium condition, Eq. (3.6a), so that the two disposable parameters in the NN-CF potential can be evaluated.

Values of R and $f_o B$(NCF) are given in columns 2 and 3, respectively, of Table IV. R and $f_o B$(NCF) for the alkali halides were computed from values of elastic constants at 0 K, which were compiled by Sangster and Atwood[33] (see their Table 5 for citations of sources), and from values of the lattice parameter at 0 K as given by Ghate.[34] R and $f_o B$(NCF) for the alkaline-earth oxides were computed from estimated harmonic values of the elastic constants and from the lattice constants at 0 K, which are tabulated in Appendix B.

Assuming that the NCF interactions involve primarily the anions, the trend in $f_o B$(NCF) with the separation of the anions, $r_{--}=r_{\mathrm{NNN}}=a\sqrt{2}$, was examined for each type of anion. $f_o B$(NCF) is plotted versus the NN equilibrium bond length a for each of the series of halides and for the oxides in Fig. 2. For a given anion, $f_o B$(NCF) generally decreases toward larger values of the bond length—that is, toward the compounds with the larger cations in each series.

For the chlorides, bromides, and iodides, the values of $f_o B$(NCF) are small, and the trends of these values are

TABLE IV. Force constants, in J/m^2.

	R Eq. (7.9)	f_0B(NCF) Eq. (7.6)	F^* Eq. (7.14)	R^* Eq. (7.21)	R^*(NCF) Eq. (7.19)
		(a) Alkali halides			
LiF	83.6	4.49	81.0	93.2	9.6
LiCl	53.9	1.07	44.8	48.7	−5.2
LiBr	42.9	1.25	35.3	40.3	−2.6
LiI				29.7	
NaF	70.82	1.398	75.7	87.8	17.0
NaCl	44.51	0.58	44.5	50.1	5.6
NaBr	40.01	0.25	37.6	42.4	2.4
NaI	34.22	−0.05	30.0	33.7	−0.5
KF	54.4	−0.04	56.3	63.7	9.3
KCl	36.8	0.38	38.5	43.7	6.9
KBr			34.8	39.2	
KI	26.7	0.52	30.2	33.5	6.8
RbF	50.41	−0.845	49.4	55.0	4.6
RbCl	36.47	−0.508	36.4	40.8	4.3
RbBr	32.81	−0.223	32.5	36.3	3.5
RbI	28.5	−0.25	28.4	31.6	3.1
		(b) Alkaline-earth oxides			
MgO	213.6	13.64	225.5	-3.4×10^4	
CaO	176.6	4.64	144.1	251.9	75.3
SrO	140.3	3.85	113.6	177.7	37.4
BaO	105	1.4	(73)	(87)	(−18)

very similar. f_0B(NCF) decreases more rapidly for the fluorides and most rapidly for the oxides. These trends suggest that for the oxides the short-range repulsive interactions contribute significantly to f_0B(NCF); whereas, for the chlorides, bromides, and iodides, van der Waals–type interactions make the major contributions to f_0B(NCF). The oxide data can be approximated very well (correlation coefficient, −0.98) by an expression

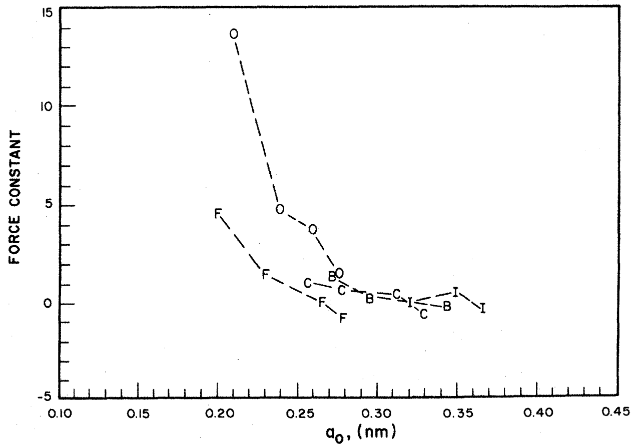


FIG. 2. f_0B(NCF) vs NN equilibrium bond length, a_0. Fluorides are indicated by F; chlorides, by C; bromides, by B; iodides, by I; and oxides, by O.

$$f_0B(\text{NCF})=f_0B_0(\text{NCF})\exp(-r_{\text{NNN}}/\rho)\,, \qquad (7.12)$$

with values of 12 920 J/m^2 for f_0B_0(NCF) and 0.0434 nm for ρ. This value of ρ compares favorably with values of $\rho(O^{2-}:O^{2-})$ computed by Mackrodt and Stewart, as quoted by Harding,[35] which range from 0.0384 for MgO to 0.0426 for BaO.

Vukcevich[5] assumed that the angle-bending function had a Gaussian dependence on the sine of the angular deviation; see his Eq. (8). Exponential functions of ionic separation, which resemble the Born-Mayer functions for overlap repulsion, were assumed by Sarkar and Sengupta[10] for the three-body interaction term of the deformable shell model of Basu and Sengupta[9] and by Buecher[7] for aligned and angular triples; see his Eqs. (5) and (6) and Fig. 5. Monopole-quadrupole interactions[11,12] and triple-dipole interactions[13,15] have been suggested as important three-body–type van der Waals interactions. The relationships between various model potentials for NCF interactions and the BDM coupling constants will be considered further in a subsequent paper.

The internal strain which results when the lattice is homogeneously polarized introduces one further condition. In the limit of long wavelength, wave vector $\vec{k}\rightarrow\vec{0}$ a transverse electric field $\vec{E}_T$ causes the oppositely charged sublattices to be displaced rigidly antiparallel to one another, whereas a longitudinal field $\vec{E}_L$ causes the sublattices to be displaced rigidly against one another. Since the lattice strains are absent in the limit of long waves, the matrix $\underline{J}$ of lattice-transformation coefficients reduces to the identity matrix $\underline{I}$, and the Born-Huang internal strain $\vec{\overline{w}}$, given by Eq. (2.16), reduces to the internal strain $\vec{w}$, given by Eq. (2.15).

The polarization of the lattice associated with the internal strain is

$$\vec{P}_D=(eZa/\Omega_c)\vec{w}\ , \tag{7.13}$$

which can be expressed as a sum of ionic displacement dipoles located on the lattice sites. The total polarization $\vec{P}$ is the sum of $\vec{P}_D$ and terms from the electronic dipole moments of the ions and from the "distortion dipoles" produced by the mutual distortion of the electronic charge clouds on neighboring ions when the ions are displaced.[36,37] The product of $\vec{P}$ with the macroscopic field $\vec{E}$ in the crystal yields the long-range, electrostatic contribution to the change in the internal energy as the result of the internal strains.

The second-order derivatives of the short-range part of the internal energy with respect to the internal strain components yield a force constant R^* for the long-wavelength limit of the optic modes. A second force constant F^*, which is equal to R^* under the special conditions of rigid ions and NN central forces, is given by the Szigeti relation[36]

$$\overline{M}\omega_0^2[\epsilon(0)+2]/[\epsilon(\infty)+2]=F^*\ . \tag{7.14}$$

In Eq. (7.14), $\overline{M}$ is the reduced mass; $\epsilon(0)$ and $\epsilon(\infty)$ are the low- and high-frequency dielectric constants, respectively; and ω_o is the optic mode frequency.

For a lattice with all ions at sites having a center of symmetry, the lattice is unpolarized in the absence of a field so that

$$U_{,w}=\partial U/\partial w=0\ . \tag{7.15}$$

Since $\partial U/\partial E_i \sim P_i$ and $w_i \sim E_i$, $U_{,ww}$ must transform like the dielectric susceptibility tensor which for cubic symmetry is isotropic. Thus it is only necessary to evaluate a single component, $U_{,11}$, of $U_{,ww}$. This second-order term in w can be obtained by substituting Eqs. (2.19a)–(2.19d) into Eq. (6.2). From Table III we find that the nonzero h-coupling constants are $h(\alpha,\overline{\alpha};\alpha,\overline{\alpha})$, $h(\alpha,\overline{\beta};\alpha,\overline{\beta})$, and $h(\alpha,\overline{\beta};\overline{\beta},\gamma)$. It is important to recognize that

$$\begin{aligned} h(\alpha,\overline{\alpha};\alpha,\overline{\alpha})&=h(\overline{\alpha},\alpha;\overline{\alpha},\alpha)=h(\alpha,\overline{\alpha};\overline{\alpha},\alpha)\\ &=h(\overline{\alpha},\alpha;\alpha,\overline{\alpha})\ , \end{aligned} \tag{7.16a}$$

$$h(\alpha,\overline{\beta};\alpha,\overline{\beta})=h(\overline{\alpha},\beta;\overline{\alpha},\beta)\ , \tag{7.16b}$$

$$\begin{aligned} h(\overline{\alpha},\beta;\alpha,\overline{\beta})&=h(\alpha,\overline{\beta};\overline{\alpha},\beta)=h(\overline{\alpha},\beta;\overline{\beta},\gamma)\\ &=h(\alpha,\overline{\beta};\beta,\overline{\gamma})=h(\overline{\alpha},\beta;\beta\overline{\gamma})=0\ . \end{aligned} \tag{7.16c}$$

After carrying out the summations over the bond indices with the aid of the summation formulas in Appendix A, and after summing over the central-atom index ν, the second-order internal strain energy term can be differentiated with respect to w_1 to obtain

$$\begin{aligned} \Omega_c U_{,ww}=6h(\alpha,\alpha)a-4[&h(\alpha,\overline{\alpha};\alpha,\overline{\alpha})+2h(\alpha,\overline{\beta};\alpha,\overline{\beta})\\ &+2h(\alpha,\overline{\beta};\overline{\beta},\gamma)]a^2 \end{aligned} \tag{7.17}$$

for the second-order derivative $U_{,ww}$. A force constant R^* can be defined as

$$R^*=\Omega_c U_{,ww}/a^2\ . \tag{7.18}$$

R^* can be expressed in terms of the f-coupling constants by use of the relationships in Table III. Using Eqs. (7.6) and (7.9) to replace some of the coupling constants by empirically determined coefficients, we obtain

$$R^*=R+R^*(\mathrm{NCF})\ , \tag{7.19}$$

where

$$R^*(\mathrm{NCF})=-8(f_{SS}^{(1b)}-8f_{BB}^{(1a)}+8f_{BB}^{(2a)}-24g_{SS}^{(1a)})\ . \tag{7.20}$$

Although R^*(NCF) contains four NCF terms, it is possible that one or more of these terms are negligible for practical materials. An examination of this possibility requires the estimation of R^* both from dielectric and from elastic constant data.

As first noted by Lyddane *et al.*,[38] the ions in a real material are deformable, which implies that the polarization of the ions will modify the short-range forces between the ions. Consequently, R^* must be obtained from F^* by a model which relates the ionic polarizabilities to the short-range force constant, such as one of the shell models—see reviews by Cochran[25] and by Basu *et al.*[26]—or the deformation dipole model.[23] We confine our discussion to an estimate of R^* from F^* using the shell-model equation[39]

$$F^*=(1/R^*+1/K_1+1/K_2)^{-1}\ , \tag{7.21}$$

where K_1,K_2 are the shell-core force constants.

Values of F^* and R^* are given in columns 4 and 5, respectively, of Table IV. These values were obtained from the work of Sangster *et al.*[39] who used the low-temperature experimental data compiled by Lowndes and Martin.[40] F^* for the alkaline-earth oxides was computed according to Eq. (7.21) from data compiled in Appendix B. Since the optic mode frequency ω_o for BaO was estimated, the values of F^* and R^* are enclosed in parentheses for this compound. The values of R^* for the alkaline-earth oxides were computed according to Eq. (7.21) using the values of the shell-core force constants computed by Mackrodt as quoted by Harding.[35] The very large and negative value of R^* for MgO suggests either that the simple shell model breaks down for MgO or that the assumption that $1/K(\mathrm{Mg})=0$, made only in the case of MgO, is untenable.

Values of R^*(NCF), in column 6 of Table IV, were calculated from R^* and R, columns 5 and 1, respectively. It is evident in comparing f_oB(NCF) and R^*(NCF) that there is little correlation between these values. The correlation coefficient for the alkali halides is 0.25. As shown in Fig. 2, for a given anion f_oB(NCF) generally decreases as the NN bond length increases—that is, as the cation size increases. This is not the case for R^*(NCF). This comparison suggests that more than one significant NCF interaction is present in the alkali halides and the alkaline-earth oxides.

Since the number of NCF coupling constants exceeds the number of empirical parameters and phenomenological constraints, an estimate of these undefined coupling constants requires recourse to models which interpret the coupling constants in terms of known parameters, such as those for the short-range CF potentials and for the atomic polarizabilities. To relate the atomic polarizabilities to the BDM coupling constants, it appears that the "distortion dipoles" also may be expanded in the bond-deformation parameters. Further constraints may be introduced by expressing the NCF coupling constants in terms of a model for multipole interactions or for three-body interactions.

VIII. SUMMARY

The BDM is an effective means of phenomenologically describing short-range interactions and can efficiently account for multiple interactions in an expansion of the strain energy in variables called "bond-deformation parameters." The coefficients, or coupling constants, of this expansion were examined in detail here for the complex of the six NN atoms about a central atom in a rocksalt-type crystal. Relationships were obtained between these coupling constants and derivatives of NN and NNN central-force potentials, the elastic constants, and the force constant for homogeneous internal strain (polarization) of the lattice.

By considering the short-range interactions in the detail permitted by the BDM, a variety of noncentral force interactions was shown to be possible. Since the BDM introduces more coupling constants than can be evaluated from empirical data, either simplifying assumptions or theoretical estimates of coupling constants are required. In either case, the present BDM indicates the interactions which either must be neglected or must be calculated. Two heuristic assumptions were introduced, Eqs. (5.22) and (7.11), to obtain an expression for the bulk modulus, $\mathscr{B}$, which contained only derivatives of NN and NNN central-force potentials.

By comparing estimates of the force constant for homogeneous polarization of the lattice, it was shown that these force constants for the alkali halides contain noncentral force terms in addition to those introduced when an adjustment is made for the Cauchy discrepancy $(C_{44}-C_{12})$.

Since the BDM as originally formulated by Keating[16] was not convenient for an introduction of its short-range forces into a lattice-dynamical treatment, a transformation was presented here which yields a new set of bond-deformation parameters and a corresponding set of coupling constants. The new bond-deformation parameters are easily related to the atomic displacements. The harmonic approximation of the short-range potential, which is obtained by expanding in these new parameters, contains seven coupling constants: a first-order coupling constant $h(\alpha\bar{\alpha})$, six symmetric second-order coupling constants, and six asymmetric coupling constants. Expressions for the first-order constants and for the symmetric second-order constants are given in Table III. These four constants can be obtained from the condition for equilibrium and the elastic constants. The analogous asymmetric constants can be obtained from the symmetric constants by assuming that only interactions centered on the anions give rise to NNN central force and NCF terms or by using appropriate model potentials to estimate these coupling constants.

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APPENDIX A: DERIVATIVES OF THE BOND-DEFORMATION PARAMETERS

Three derivatives of $\lambda(\alpha,\beta;\nu)$ with respect to the strains can be obtained from Eq. (2.18):

$$H_{kl}(\alpha,\beta;\nu)=\left.\frac{\partial\lambda(\alpha,\beta;\nu)}{\partial\eta_{kl}}\right|_0$$

$$=[(\alpha\nu;k)(\beta\nu,l)+(\alpha\nu,l)(\beta\nu;k)]a\ , \tag{A1a}$$

$$W_k(\alpha,\beta;\nu)=\left.\frac{\partial\lambda(\alpha,\beta;\nu)}{\partial\bar{w}_k}\right|_0$$

$$=[(\alpha\nu;k)+(\beta\nu,k)]a\ , \tag{A1b}$$

$$W_{kl}(\alpha,\beta;\nu)=\left.\frac{\partial^2\lambda(\alpha,\beta;\nu)}{\partial\bar{w}_k\partial\bar{w}_l}\right|_0$$

$$=2a\delta_{kl}\ , \tag{A1c}$$

where

$$(\alpha\nu;k)\equiv x_k(\alpha,\nu)/a\ . \tag{A2}$$

Values of $(\alpha\nu,k)$ are given in Table V. Also, from Eqs. (2.19a)–(2.19d), we obtain

$$W_{kl}(\alpha,\beta;\nu)=\left.\frac{\partial^2\mu(\alpha,\beta;\nu)}{\partial\bar{w}_k\partial\bar{w}_l}\right|_0 , \tag{A3a}$$

$$H_{kl}(\alpha,\beta;\nu)=\left.\frac{-\partial\mu(\bar{\alpha},\bar{\beta};\nu)}{\partial\eta_{kl}}\right|_0 , \tag{A3b}$$

$$W_k(\alpha,\beta;\nu)=ia\left.\left[\frac{\partial\mu(\alpha,\bar{\beta};\nu)}{\partial\bar{w}_k}+\frac{\partial\mu(\bar{\alpha},\beta;\nu)}{\partial\bar{w}_k}\right]\right|_0 . \tag{A3c}$$

It is evident from the values in Table V that

TABLE V. Values of the coefficients $(\alpha\mu,k)$ for NN bonds.

k/α	1	2	3	4	5	6
1	1	0	0	-1	0	0
2	0	1	0	0	-1	0
3	0	0	1	0	0	-1

$$\sum_{\alpha=1}^{3}(\alpha\nu,k)=1\ , \tag{A4a}$$

$$\sum_{\alpha=4}^{6}(\alpha\nu,k)=-1\ , \tag{A4b}$$

$$\sum_{\alpha=1}^{3}(\alpha\nu,k)^2=\sum_{\alpha=4}^{6}(\alpha\nu,k)^2=1\ . \tag{A4c}$$

Equation (A4b) follows from $x_k(\bar{\alpha},\nu)=-x_k(\alpha,\nu)$ so that from Eq. (A2)

$$(\bar{\alpha}\nu,k)=-(\alpha\nu,k)\ . \tag{A5}$$

Since $(\alpha\nu_A,k)=(\alpha\nu_B,k)$, it follows that the derivatives $H_{kl}(\alpha,\beta;\nu)$, $W_k(\alpha,\beta;\nu)$, and $W_{kl}(\alpha,\beta;\nu)$ are independent of the basis index ν, so that the basis designation can be omitted from these derivatives. It follows from Eq. (A4c) that the summation, in which α runs over NN bonds which are perpendicular to a NN bond ϵ, is

$$\sum_{\alpha\perp\epsilon}(\alpha\nu,k)^2=2[1-(\epsilon\nu,k)^2]\ . \tag{A6}$$

Derivatives of the bond-deformation parameters with respect to the relative coordinates of the displaced atoms are required to relate the BDM coupling constants to derivatives of the interatomic potentials. It follows from Eq. (2.3) that differentiation of $\lambda(\alpha,\beta;\nu)$ with respect to $x_i'(\epsilon,\nu)$ is equivalent to differentiating with respect to $u_i(\epsilon,\nu)$. The first and second derivatives of $\lambda(\alpha,\beta;\nu)$ with respect to components of relative displacements of NN atoms are

$$X_i(\alpha,\beta;\epsilon;\nu)=\left.\frac{\partial\lambda(\alpha,\beta;\nu)}{\partial x_i(\epsilon,\nu)}\right|_0$$

$$=(\alpha\nu,i)\delta_{\beta\epsilon}+(\beta\nu,i)\delta_{\alpha\epsilon}\ , \tag{A7a}$$

$$X_{ij}(\alpha,\beta;\epsilon,\zeta;\nu)=\left.\frac{\partial^2\lambda(\alpha,\beta;\nu)}{\partial x_i'(\epsilon,\nu)\partial x_j'(\zeta,\nu)}\right|_0$$

$$=(\delta_{\alpha\epsilon}\delta_{\beta\zeta}+\delta_{\alpha\zeta}\delta_{\beta\epsilon})\delta_{ij}/a\ . \tag{A7b}$$

APPENDIX B: EMPIRICAL COEFFICIENTS FOR THE ALKALINE-EARTH OXIDES

We present empirical coefficients for the alkaline-earth oxides computed from estimated harmonic values of the elastic constants and from the lattice constants at 0 K. References to experimental data are given below table.

Empirical coefficients for the alkaline-earth oxides.

	MgO	CaO	SrO	BaO
a(0 K), nm	0.2099[a,b]	0.2394[c,d]	0.2569[e,f]	0.2759[g,h]
c_{11} (harmonic), GPa	315.9[i]	242.5[c,j]	187[j,k]	122[l]
c_{12} (harmonic)	96.5	62.8	43	34
c_{44} (harmonic)	161.5	82.6	58	39
$\epsilon(0)$	9.782[m]	11.1[n]	13.1[n]	34[o]
$\epsilon(\infty)$	2.945[p,q]	3.33[p]	3.46[p]	3.558[p]
ω_0, THz	76.85[q]	55.57[n]	42.76[n]	21.7[r]

[a] Density, Ref. 41.
[b] Thermal expansion, Ref. 42.
[c] Density; elastic constants, Ref. 43.
[d] Thermal expansion, Ref. 44.
[e] Lattice parameter, Ref. 45.
[f] Thermal expansion, Ref. 46.
[g] Lattice parameter, Ref. 47.
[h] Thermal expansion, Ref. 48.
[i] Elastic constants and temperature derivatives, Ref. 49.
[j] Temperature derivatives of elastic constants, Ref. 50.
[k] Elastic constants, Ref. 51.
[l] Elastic constants and temperature derivatives, Ref. 52.
[m] Static dielectric constant, Ref. 53.
[n] Static dielectirc constant, Ref. 54.
[o] Static dielectric constant, Ref. 55.
[p] High-frequency dielectric constant, Ref. 56.
[q] Temperature dependence of high-frequency dielectric constant, Ref. 57.
[r] Estimated.

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[1] Although noncentral-force interactions are MB—that is, they involve three or more atoms; MB interactions may be central force if the interactions are between centers of atoms; see Sec. III. Unless otherwise indicated, MB interactions will be included, however, in the category of noncentral-force interactions since central-force interactions have been traditionally restricted to pairwise interactions.

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