(a) Electronic

Omitted because this experiment was not performed.

(b) Atomic

$$n_{ba}=2N(2\mathcal{B}_{ac}+\mathcal{B}_{ad})/(2\mathcal{B}_{ac}+2\mathcal{B}_{ab}+\mathcal{B}_{ad}+\mathcal{B}_{bc})\quad(=n_{bc}=n_{bd}),$$

$$n_{ca}=2N(2\mathcal{B}_{ab}+\mathcal{B}_{ad})/(2\mathcal{B}_{ac}+2\mathcal{B}_{ab}+\mathcal{B}_{ad}+\mathcal{B}_{bc})\quad(=n_{cb}=n_{cd}),$$

$$n_{ab}=2N(\mathcal{B}_{bc}+\mathcal{B}_{ac}+\mathcal{B}_{ab})/(2\mathcal{B}_{ac}+2\mathcal{B}_{ab}+\mathcal{B}_{ad}+\mathcal{B}_{bc})\quad(=n_{ac}=n_{ad}=n_{da}=n_{db}=n_{dc}),$$

4. [110] Stress

(a) Electronic

$$n_{ad}=3N\mathcal{B}_{bc}/(\mathcal{B}_{bc}+2\mathcal{B}_{cd})\quad(=n_{da}),$$

$$n_{ab}=3N\mathcal{B}_{cd}/(\mathcal{B}_{bc}+2\mathcal{B}_{cd})\quad(=n_{ac}=n_{db}=n_{dc}),$$

$$n_{bc}=3N\mathcal{B}_{ad}/(\mathcal{B}_{ad}+2\mathcal{B}_{cd})\quad(=n_{cb}),$$

$$n_{ba}=3N\mathcal{B}_{cd}/(\mathcal{B}_{ad}+2\mathcal{B}_{cd})\quad(=n_{bd}=n_{ca}=n_{cd}).$$

(b) Atomic

$$n_{ab}=2N(2\mathcal{B}_{cd}+\mathcal{B}_{bc})/(\mathcal{B}_{bc}+4\mathcal{B}_{cd}+\mathcal{B}_{ad})\quad(=n_{ac}=n_{ad}=n_{da}=n_{db}=n_{dc})$$

$$n_{ba}=2N(2\mathcal{B}_{cd}+\mathcal{B}_{ad})/(\mathcal{B}_{bc}+4\mathcal{B}_{cd}+\mathcal{B}_{ad})\quad(=n_{bc}=n_{bd}=n_{ca}=n_{cb}=n_{cd}).$$

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Relationship between the Macroscopic and Microscopic Theory of Crystal Elasticity. I. Primitive Crystals

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The general relationship between the macroscopic theory of crystal elasticity and a recently introduced microscopic formalism is established for primitive crystals. The relationship is more simple and direct than the corresponding relationship between the macroscopic theory and the Born-Huang formalism, which has to be established via sound-wave propagation. Additional conditions are derived for the Born-Huang formalism which remove an inconsistency in the microscopic theory and confirm that purely nearest-neighbor interactions must be central. The new macroscopic-microscopic relationship is applied to an illustrative study of the simple cubic structure which also shows that three of the six third-order elastic constants of the alkali halides depend on long-range interactions.

I. INTRODUCTION

The Born-Huang coupling-parameter formulation[1] of microscopic elasticity has been in use for some time, and its relationship with the macroscopic formalism has been examined in several articles.[1,2] Recently, a new formalism[3] has been set up for microscopic elasticity which allowed the formal demonstration that a purely nearest-neighbor interaction must be a central one.[3] The new approach offers a number of operational advantages over the Born-Huang formalism which have been demonstrated in calculations of the second-[3] and third-order[4] elasticity of crystals of the diamond type. Thus it has now become advisable to establish the general relationship between this new microscopic approach and the macroscopic formalism so that it can be used more generally. The general relationship is set up for the case of primitive crystals in the present article; the case of nonprimitive crystals exhibits special problems and will be considered in a separate article. We shall show here that, in addition to the advantages mentioned in previous articles,[3,4] the new formulation of macroscopic elasticity allows a more simple and direct formal relationship between macroscopic and microscopic elasticity for primitive crystals than is possible with the Born-Huang approach.

There has also arisen a second problem in the study of the microscopic theory of elasticity. In Ref. 3, hereafter referred to as K, purely first-neighbor interactions were shown to be central. Because the two approaches begin on common ground and are designed to allow the same invariance requirements to be imposed, they should be basically equivalent. However, for certain crystal structures of high symmetry, the Born-Huang

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[1] M. Born, K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chap. V.

[2] See, for example, M. Lax, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 583; G. Leibfried and W. Ludwig, Z. Physik **160**, 80 (1960); R. Srinivasan, Phys. Rev. **144**, 620 (1966).

[3] P. N. Keating, Phys. Rev. **145**, 637 (1966).

[4] P. N. Keating, Phys. Rev. **149**, 674 (1966).

approach allows the existence of a noncentral purely nearest-neighbor interaction, in contradiction to the result obtained in K. This inconsistency will be examined in some detail and certain inadequacies in the present Born-Huang approach will be demonstrated. We shall find that additional conditions must be imposed in the case of primitive crystals.

In the next section, we shall introduce the new approach as a general formalism for primitive structures and establish the formal relationship between it and the macroscopic theory. In the third section, we shall compare and contrast the new formalism with the Born-Huang approach and examine the latter critically. Finally, we shall show how the microscopic-macroscopic relationship applies to specific primitive crystals by an illustrative study of the second and third order elasticity of the simple cubic type of crystal.

This article is restricted to nonmetallic crystals and also to nonpiezoelectric solids. However, this latter imposes no additional restrictions, for all primitive crystals are nonpiezoelectric.

II. THE MICROSCOPIC-MACROSCOPIC RELATIONSHIP

Both microscopic approaches begin by assuming the elastic strain energy V of a crystal is a function only of the nuclear positions $\mathbf{x}_k$. Such an assumption relies on the Born-Oppenheimer approximation, valid for nonmetallic crystals. Because this strain energy must be invariant under a rigid displacement of the crystal, it can depend only on the *differences* in nuclear position $\mathbf{x}_{kl}=\mathbf{x}_k-\mathbf{x}_l$. However, V must be invariant under the full Euclidean group and therefore also under an arbitrary rigid rotation. Hence, V must be a function of the invariants under such a transformation which can be formed from the $\mathbf{x}_{kl}$. The only invariants under the full orthogonal group are the scalar products $\mathbf{x}_{kl}\cdot\mathbf{x}_{mn}$ and functions of such products.[5] Thus we define the invariants

$$\lambda_{klmn}=(\mathbf{x}_{kl}\cdot\mathbf{x}_{mn}-\mathbf{X}_{kl}\cdot\mathbf{X}_{mn})/2a_0,$$

where $\mathbf{X}_{kl}$ is the value of $\mathbf{x}_{kl}$ at the zero-stress configuration and a_0 is a unit-cell dimension. The strain energy must be a function $V=V(\lambda_{klmn})$ of these invariants.[3]

However, the set of λ_{klmn} is not an independent set since only $3N$-6 invariants are needed to specify an arrangement of N points displaced only slightly from a known configuration. The problem of finding an independent set of invariants was tackled in K, and it was shown how such an independent set can be obtained for primitive crystals. However, these invariants are not distributed uniformly throughout the crystal[3] and are thus somewhat inconvenient to use. It was shown in K that no distinctly different scalar products, or products of them, arise in the bulk if a somewhat larger set is used which has the advantage of being uniformly distributed. Thus, if $\mathbf{x}_1(l)$, $\mathbf{x}_2(l)$, $\mathbf{x}_3(l)$ are the relative position vectors of the three nuclei adjacent to the nucleus in cell (l) which are mutually adjacent,[3] (see Fig. 1) then

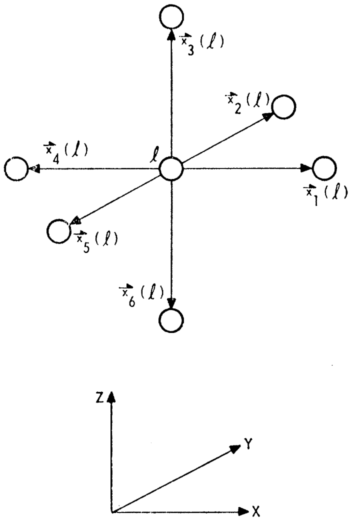

FIG. 1. Labeling of the six first neighbors of the atom belonging to cell (l) in the simple cubic structure.

$$V=\sum_l\sum_{m,n=1}^{3}A_{mn}\lambda_{mn}(l)$$
$$+\tfrac{1}{2}\sum_{l,l'}\sum_{\substack{m,n\\m',n'}}^{3}B_{mnm'n'}(l-l')\lambda_{mn}(l)\lambda_{m'n'}(l')+\cdots,\quad(1)$$

for the strain energy of the bulk of large, primitive crystals, where

$$\lambda_{mn}(l)=(\mathbf{x}_m(l)\cdot\mathbf{x}_n(l)-\mathbf{X}_m\cdot\mathbf{X}_n)/2a_0.$$

The term linear in the λ_{mn} can readily be shown to vanish although, for reasons of generality, it will be retained for the moment. The coefficients in this expansion are independent but for crystal symmetry requirements.

The λ_{mn} are symmetric in the interchange of m, n and thus $A_{mn}=A_{nm}$, $B_{mnm'n'}=B_{nmm'n'}$, etc. Furthermore, the B coefficients are coefficients of a quadratic form and thus symmetric in the sense

$$B_{mnm'n'}(l-l')=B_{m'n'mn}(l'-l),$$

but we note that $B_{mnm'n'}\neq B_{m'nmn'}$, in general.

If the concept of crystal elasticity is to be of use, the deformation must be sufficiently slowly varying so that it may be considered uniform over several unit cells. In this case, we may define an energy density U in the bulk from Eq. (1). If Ω is the undeformed unit-cell

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[5] See, for example, H. Weyl, *The Classical Groups* (Princeton University Press, Princeton, New Jersey, 1939), theorem $T_n{}^m$ in Sec. 9. The "odd invariants," such as the pseudoscalar $\mathbf{x}_{ij}\cdot(\mathbf{x}_{kl}\times\mathbf{x}_{mn})$, are not invariants under the improper subgroup of the orthogonal group.

volume,

$$\Omega U(l)=\sum_{m,n} A_{mn}\lambda_{mn}(l)+\tfrac{1}{2}\sum_{l'}\sum_{\substack{m,n\\m',n'}} B_{mnm'n'}(l-l')\times\lambda_{mn}(l)\lambda_{m'n'}(l')+\tfrac{1}{6}\sum_{l',l''}\sum C_{mnm'n'm''n''}(l,l',l'')\times\lambda_{mn}(l)\lambda_{m'n'}(l')\lambda_{m''n''}(l'')+\cdots. \quad (2)$$

This allows a much more direct relation between microscopic and macroscopic elasticity than is possible with the Born-Huang approach. In the Born-Huang formalism, it is not possible to define an energy density under homogeneous deformation because, in this approach, the surface makes a contribution proportional to the crystal volume, as Lax has shown.[2] Equation (2) is valid for cells (l) which are an appreciably greater distance from the surface than the range of the interactions; the vast majority of the cells are of this type in large, primitive crystals.

The lattice stability condition (i.e., V and U are *minima* at the equilibrium, zero-stress condition) requires that $\{A\}$ vanishes and $\{B\}$ is positive definite. Because V and U cannot depend linearly on the $u_m{}^\alpha$, where $\mathbf{u}_m=\mathbf{x}_m-\mathbf{X}_m$, we require

$$\sum_n A_{mn}X_n{}^\alpha=0 \quad \text{for} \quad m=1,\,2,\,3;\quad \alpha=1,\,2,\,3.$$

Thus (A_{mn}) is a 3×3 symmetric matrix with three vanishing eigenvalues and is therefore null, $A_{mn}=0$.

The $\{B\}$ and $\{C\}$ sets of coefficients must be invariant under the space group of the crystal. The invariance of the $\{B\}$ and $\{C\}$ sets of coefficients under the quotient (i.e., symmetry) subgroup means that, in general, more nuclei contribute to the sums in Eq. (2) than those connected to the reference nuclei by the vectors $\mathbf{x}_1$, $\mathbf{x}_2$, $\mathbf{x}_3$. For example, all primitive crystals have site inversion symmetry and hence the sum of quadratic terms in Eq. (2), $\frac{1}{2}\sum_1{}^3\cdots$, becomes $(\frac{1}{4}\sum_1{}^3\cdots+\frac{1}{4}\sum_{-3}{}^{-1}\cdots)$, where $-n$ refers to the nucleus at $-\mathbf{X}_n$ in the equilibrium configuration. In many crystals, there will be further symmetry which will introduce additional terms but we note that this does not introduce more coefficients; the final set of coefficients is still, of course, an independent one. These points will be examined further in Sec. IV.

Because of the similar way in which they are defined, the variables of the new microscopic theory are closely related to the macroscopic strain variables[1,2]

$$\eta_{\alpha\beta}=\tfrac{1}{2}(x^\gamma{}_{,\alpha}x_{\gamma,\beta}-\delta_{\alpha\beta}),$$

where the summation convention is used and where $x^\alpha{}_{,\beta}=\partial x^\alpha/\partial X^\beta$, if $\mathbf{x}$, $\mathbf{X}$ are the positions of a point in the continuum after and before deformation, respectively. For slowly varying strains in primitive crystals,

$$\lambda_{mn}(l)=\frac{1}{2a_0}X_m{}^\alpha X_n{}^\beta(x^\gamma{}_{,\alpha}x_{\gamma,\beta}-\delta_{\alpha\beta})=\frac{1}{a_0}\eta_{\alpha\beta}X_m{}^\alpha X_n{}^\beta, \quad (3)$$

where $X_m{}^\alpha$ is the αth component of $\mathbf{X}_m$. If we substitute this expression for λ_{mn} into Eq. (2), we obtain

$$\Omega U=\tfrac{1}{2}B_{mnm'n'}(l-l')\eta_{\alpha\beta}(l)\cdot\eta_{\alpha'\beta'}(l')\times X_m{}^\alpha X_n{}^\beta X_{m'}{}^{\alpha'}X_{n'}{}^{\beta'}+\cdots. \quad (4)$$

We shall consider only the case in which the deformations are sufficiently slowly varying so that $\eta_{\alpha\beta}$ does not vary appreciably over the interaction range and thus $\eta_{\alpha\beta}(l)=\eta_{\alpha\beta}(l')$ in Eq. (4). This is the usual situation in macroscopic elasticity. On the other hand, Toupin[6] has extended the macroscopic formalism to include the additional contributions to U from the second derivatives $x^\gamma{}_{,\alpha\beta}$ and it is possible to also evaluate the additional macroscopic coefficients thereby introduced in terms of the microscopic B and C coefficients. This will not, however, be undertaken here.

Hence, if $\eta_{\alpha\beta}(l')=\eta_{\alpha\beta}(l)$ in Eq. (4), we obtain expressions for the macroscopic elasticity coefficients when Eq. (4) is compared with the Brugger macroscopic energy density[7]:

$$c_{\alpha\beta}=\frac{1}{\Omega a_0}A_{mn}X_m{}^\alpha X_n{}^\beta=0,$$

$$c_{JK}\equiv c_{\alpha\beta\alpha'\beta'}=\frac{1}{\Omega a_0{}^2}\sum_{l'}B_{mnm'n'}(l-l')\times X_m{}^\alpha X_n{}^\beta X_{m'}{}^{\alpha'}X_{n'}{}^{\beta'}, \quad (5)$$

$$c_{JKL}\equiv c_{\alpha\beta\alpha'\beta'\alpha''\beta''}=\frac{1}{\Omega a_0{}^3}\sum_{l',l''}C_{mnm'n'm''n''}(l,l',l'')\times X_m{}^\alpha X_n{}^\beta X_{m'}{}^{\alpha'}X_{n'}{}^{\beta'}\times X_{m''}{}^{\alpha''}X_{n''}{}^{\beta''},$$

where the c_{JK}, c_{JKL} are the second- and third-order elasticity coefficients of Brugger.[7]

We note that the relations between the elasticity coefficients and the microscopic coefficients are simple and elegant and that the different orders are uncoupled, i.e., there are no B contributions to c_{JKL}, for example. The generalization to fourth, and higher, orders is obvious. The above relationship between microscopic and macroscopic elasticity is much more direct than for the Born-Huang theory, especially when third-order (i.e., anharmonic) effects are to be considered. The main reasons for this are that the new microscopic variables are closely related to the macroscopic strain variables and an energy density can be defined. The complexity associated with the Born-Huang approach is graphically demonstrated in Srinivasan's article,[2] albeit for nonprimitive crystals.

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[6] R. A. Toupin, Arch. Ratl. Mech. Anal. **11**, 385 (1962); R. A. Toupin and D. C. Gazis, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press Inc., New York, 1965), p. 597.

[7] K. Brugger, Phys. Rev. **133**, A1611 (1964).

III. THE RELATIONSHIP WITH THE BORN-HUANG THEORY

The Born-Huang formalism[1] begins by assuming that the strain energy can be written as a series expansion in the components of the nuclear displacements, u_m^α, from equilibrium

$$V=V_0+\tfrac{1}{2}\sum K_{mn}^{\alpha\beta}u_m^\alpha u_n^\beta+\cdots, \tag{6}$$

where the linear term vanishes because of the equilibrium condition. The requirement that V is invariant under the operations of the Euclidean group is imposed by means of conditions on the coefficients $K_{mn}^{\alpha\beta}$. For example, displacement invariance requires that[1,2]

$$\sum_m K_{mn}^{\alpha\beta}=0, \tag{7}$$

and rotational invariance requires[1,2]

$$\sum_m K_{mn}^{\alpha\beta}X_m^\gamma \tag{8}$$

be symmetric in (α,γ). The newer formalism can also be reduced to the form (6) if only the linear terms in the nuclear displacements are retained in the λ_{mn}. The $K_{mn}^{\alpha\beta}$ are then linear combinations of the B coefficients. One would expect that these two forms would then be identical since the two approaches should be equivalent. However, as already mentioned, the Born-Huang conditions (7), (8) do not always exclude noncentral nearest-neighbor forces, in contradiction to K. This is a fundamental and important inconsistency which requires investigation.

We shall investigate the difficulty for the specific case of the simple cubic lattice. In this case, the Born-Huang conditions, together with symmetry, give rise to the nearest-neighbor force-constant matrix

$$(K_{0n})=\begin{bmatrix}\alpha_1 & 0 & 0\\ 0 & \beta_1 & 0\\ 0 & 0 & \beta_1\end{bmatrix},$$

for the nearest neighbors along the x direction and similar matrices for the other first neighbors. If we confine ourselves to a nearest-neighbor model, displacement invariance [Eq. (7)] requires

$$(K_{00})=\begin{bmatrix}\gamma & 0 & 0\\ 0 & \gamma & 0\\ 0 & 0 & \gamma\end{bmatrix},$$

where $\gamma=-2(\alpha_1+2\beta_1)$. The rotational invariance condition [Eq. (8)] imposes no conditions on the coefficients because

$$\sum_n K_{0n}^{\alpha\beta}X_n^\gamma=0,$$

because of symmetry. The central-force condition is $\beta_1=0$ and thus we see that the Born-Huang approach gives results which are in direct contradiction to the results of K. That it is the Born-Huang result which is incorrect can be seen from the following.

Because the $K_{mn}^{\alpha\beta}$ for nearest-neighbor interactions are symmetrical in (m,n) and in (α,β), the potential energy can be rewritten[8] as

$$V=-\tfrac{1}{4}\sum K_{mn}^{\alpha\beta}(u_m^\alpha-u_n^\alpha)(u_m^\beta-u_n^\beta), \tag{9}$$

which is essentially the form used by Kittel[9] in Eq. (4.33) of Ref. 9. The fact that the results of this calculation are inconsistent with those of the Born–von Kármán calculation [Eq. (4.37) of Ref. 9] has already been noted,[3] as has the lack of rotational invariance of this strain energy.[10] We can see this formally by rotating the infinite crystal rigidly from its zero-stress configuration. From Eq. (9),

$$\Delta V=-\tfrac{1}{4}\sum K_{mn}^{\alpha\beta}r_{\alpha\alpha'}r_{\beta\beta'}X_{mn}^{\alpha'}X_{mn}^{\beta'}=0$$

where $r_{\alpha\alpha'}=R_{\alpha\alpha'}-\delta_{\alpha\alpha'}$ if $(R_{\alpha\alpha'})$ represents a rigid rotation and $\mathbf{X}_{mn}=\mathbf{X}_m-\mathbf{X}_n$. The $(r_{\alpha\alpha'})$ reduces to the usual antisymmetric infinitesimal rotation matrix for infinitesimal rotations. In this case, $r_{\alpha\alpha'}=\omega_{\alpha''}\delta_{\alpha\alpha'\alpha''}$ where $\omega_{\alpha''}$ is a component of the rotation vector and $\delta_{\alpha\alpha'\alpha''}$ is the Levi-Civita density. Thus we require, using lattice translational invariance,

$$\sum_{\substack{n\\ \alpha,\beta,\alpha',\beta'}} K_{mn}^{\alpha\beta}X_{mn}^{\alpha'}X_{mn}^{\beta'}\delta_{\alpha\alpha'\alpha''}\delta_{\beta\beta'\beta''}=0, \tag{10}$$

which is an additional condition not generally satisfied by conditions (7,8). For example, in the simple-cubic case discussed above, for $\alpha''=\beta''=3$, Eq. (10) gives

$$4\beta_1a^2=0,\quad \text{i.e.,}\quad \beta_1=0,$$

where a is the nearest-neighbor distance.

Thus, there are additional rotational-invariance conditions over and above conditions (8) which, when applied, remove the inconsistency between the Born-Huang formalism and the approach introduced in K. In other words, the *corrected* Born-Huang approach also requires purely nearest-neighbor interactions to be central only.[11] If contributions from antisymmetric coefficients $K_{mn}^{\alpha\beta}$ are also included in the potential energy, however, the potential cannot be written in the form of Eq. (9) and condition (10) is then not applicable. Nevertheless, antisymmetric K coefficients do not arise in the interior of primitive crystals[2] and thus conditions (10) must always be imposed in such cases.

It is worth noting that Lax[2] suggested that rotational invariance to higher orders in the infinitesimal rotation vector might provide additional conditions on the Born-Huang force-constants; we see that this suggestion has

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[8] See Appendix A of Lax's article (Ref. 2).

[9] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956).

[10] See, for example, H. Kaplan, Phys. Rev. **125**, 1905 (1962); R. F. Wallis, Phys. Rev. **116**, 302 (1959).

[11] This is also true for nonprimitive crystals, such as those with the diamond structure, but a detailed discussion of this will be left until a separate article on the nonprimitive case.

been confirmed here. It is also interesting to note that Kaplan[10] has indicated how the zero-pressure condition can also cause purely first-neighbor noncentral terms to vanish. We do not claim that condition (10) represents *all* of the additional requirements to be included in the Born-Huang approach. Other conditions may yet be found and the Born-Huang method should be used with caution until it has been fully re-examined.[12]

IV. THE SECOND- AND THIRD-ORDER ELASTICITY OF SIMPLE-CUBIC CRYSTALS

We shall consider the elastic properties of a simple cubic crystal with only first- and second-neighbor interactions present. Thus, we shall drop all terms which connect different unit cells since these involve third and more distant neighbors. We shall include harmonic and (cubic) anharmonic interactions between nearest neighbors, which are central, and two types of second-neighbor interaction. The present calculation is intended primarily as an illustration of the application of the new formalism since most real crystals with this structure are either metals or involve long-range interactions. However, the present model could form the basis of a more general model which also includes long-range interactions.

For reasons which will become apparent below, we choose the potential energy as

$$\begin{aligned} V=\sum_{l} \tfrac{1}{2}\{ (\alpha/8a^2) \sum_{i=1}^{6} (x_{0i}^2-a^2)^2 \\ +(\beta/8a^2) \sum_{i,j<i}^{6}{}' (\mathbf{x}_{0i}\cdot\mathbf{x}_{0j})^2 \\ +(\gamma/8a^2) \sum_{l,j<i}^{6}{}' (x_{0i}^2-a^2)(x_{0j}^2-a^2)\} \\ +\tfrac{1}{6}\{\mu/8a^3) \sum_{l=1}^{6} (x_{0i}^2-a^2)^3 \\ +(\nu/4a^3) \sum_{l,j\neq i}^{6}{}' (x_{0i}^2-a^2)(x_{0j}^2-a^2)^2 \\ +(\pi/4a^3) \sum_{l,j<i}^{6}{}' (\mathbf{x}_{0i}\cdot\mathbf{x}_{0j})^2(x_{0i}^2+x_{0j}^2-2a^2)\}\,. \end{aligned} \quad (11)$$

The full crystal symmetry has been imposed on the coefficients and we see that additional terms arise, as discussed in Sec. II. The prime denotes that the terms in λ_{14}, λ_{25}, and λ_{36} (see Fig. 1) are to be excluded from the sum; these are not introduced by the symmetry conditions. We could follow the procedure used in previous calculations[3,4] and evaluate the energy density in terms of the macroscopic strain variables. However, we can now utilize the simpler method of using the general expressions (5) to evaluate the macroscopic coefficients. The second-order microscopic coefficients are

$$B_{iiii}(0)=\alpha/2\,,$$

$$B_{ijij}(0)=\beta/8=B_{ijji}(0)=B_{jiji}(0)\,,\quad (i\neq j)$$

$$B_{iijj}(0)=\gamma/4=B_{jjii}(0)\,,$$

for i, j in the range 1 to 6 ($i\neq j$).

In this case, the expression (5) for the second-order elasticity coefficients reduces to

$$c_{\alpha\beta\alpha'\beta'}=\frac{1}{a^5}\sum B_{iji'j'}(0)X_i^{\alpha}X_j^{\beta}X_{i'}^{\alpha'}X_{j'}^{\beta'}\,.$$

Hence,

$$\begin{aligned} c_{11}&=\alpha/a\,,\\ c_{12}&=\gamma/a\,,\\ c_{44}&=\beta/2a \end{aligned} \quad (12)$$

are the expressions for the three elastic constants. It is to be noted that care must be taken to ensure that all terms are included in the sum. For example, the β contribution to c_{44} is

$$\beta/8a^5 \sum_{m,n\neq m} [(X_m^3X_n^2)^2+X_m^3X_n^2X_n^3X_m^2]\,.$$

We see from Eqs. (12) that the three microscopic constants used contribute separately to the three elastic constants. The microscopic form (11) for the harmonic part of the potential energy was chosen in such a way that it can be reduced to the case of first- and second-neighbor *central* interactions. The first neighbor term is, of course, central by necessity, as demonstrated in *K* and confirmed in the present article, and a second-neighbor central interaction would involve terms such as $(x_{12}^2-X_{12}^2)^2$. Now $(1/2a)(x_{12}^2-X_{12}^2)=(\lambda_{11}+\lambda_{22}-2\lambda_{12})$ and hence the second-neighbor central interaction involves terms such as $\lambda_{11}^2+\lambda_{22}^2+2\lambda_{11}\lambda_{22}-4\lambda_{12}\times(\lambda_{11}+\lambda_{22})+4\lambda_{12}^2$. The first two terms are incorporated in α, the third term is represented in Eq. (11) by the γ terms and the last term by the β terms; it can be readily shown that there is no contribution due to the penultimate term. Thus a harmonic first and second neighbor central interaction model corresponds to the case $\beta=2\gamma$. In this case, the Cauchy relation $c_{12}=c_{44}$ is obeyed, as one would expect.

The third-order microscopic coefficients are

$$C_{iiiiii}(0)=\mu\,,$$

$$C_{ijijij}(0)=C_{iiijij}(0)=C_{iiijji}(0)=\pi/6\,,\quad (i\neq j)$$

$$C_{jjiijj}(0)=C_{iijjjj}(0)=2\nu/3\,,$$

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[12] Since this article was submitted, we have become aware of very recent work by D. C. Gazis and R. F. Wallis [Phys. Rev. **151**, 578 (1966)], who have reached similar conclusions independently. These workers obtain a set of conditions which are essentially the same as Eq. (10) of this work for the case of symmetric force constants but also obtain a more general set of conditions for which this is a special case. These additional conditions which must be imposed make the Born-Huang approach even more inconvenient to use, of course.

and the expression (5) becomes

$$c_{\alpha\beta\alpha'\beta'\alpha''\beta''}=\frac{1}{a^6}\sum C_{iji'j'i''j''}(0)$$
$$\times X_i^{\alpha}X_j^{\beta}X_{i'}^{\alpha'}X_{j'}^{\beta'}X_{i''}^{\alpha''}X_{j''}^{\beta''}.$$

Hence

$$\begin{aligned} c_{111}&=2\mu\,,\\ c_{112}&=8\nu/3\,,\\ c_{123}&=c_{144}=c_{456}=0\,,\\ c_{166}&=2\pi/3\,, \end{aligned} \tag{13}$$

are the resulting expressions for the six third-order macroscopic coefficients.

We can also write the anharmonic part of the potential energy as first- and second-neighbor central interactions. In this case, we are concerned with terms of the type $(x_{12}^2-X_{12}^2)^3$. This involves terms such as λ_{11}^3, which is incorporated in the first-neighbor anharmonic term, $3\lambda_{11}\lambda_{22}^2$ (the ν term), and $12\lambda_{11}\lambda_{12}^2$ (the π term), together with terms which are either equivalent to these (e.g., λ_{22}^3) or which do not contribute. Thus, the central interaction model corresponds to $\pi=4\nu$. Again, we find that the Cauchy relation $c_{112}=c_{166}$ is obeyed when this central interaction relation is used.

Although, as already stated, this calculation was intended primarily as an illustration of the use of the new microscopic formalism, it also sheds some light on the contributions to the third-order elasticity of the alkali halides. These crystals are not primitive, of course, but, because of the high symmetry present, there is no internal strain and their elasticity is very similar. If we compare our results with existing theoretical calculations[13] and experimental data[14,15] for crystals with the rock salt structure, we observe some interesting facts. In the present calculation, using terms out to second neighbors, the elastic constants c_{123}, c_{144}, c_{456} are zero. The experimental values of the second and third order elastic constants almost obey the Cauchy relations and thus central interactions predominate. Hence, the contributions to these elastic constants are from third-neighbor and more distant interactions and there are virtually none from first and second neighbors. This explains both the small magnitude of these three constants (because only long-range terms are involved) and their sign.[13,15] The constants c_{123}, c_{144}, c_{456} are positive, whereas the others are negative. The constants c_{112} and c_{166} are due to the second-neighbor interaction which will be predominantly repulsive since it involves ions with the same charge. However, the three constants c_{123}, c_{144}, c_{456} are due to longer-range terms of which the most important will be the third-neighbor term. This latter involves unlike ions and will therefore be attractive; hence the positive values for these constants. Furthermore, we should expect the Cauchy relation $c_{123}=c_{144}=c_{456}$ to be much better obeyed than the other Cauchy relation $c_{112}=c_{166}$ since third-neighbor interactions are likely to be more central than second-neighbor interactions. There will also be small four-body second-neighbor contributions to these elastic constants but these will be noncentral and will account only for the small deviations from the Cauchy relations.

V. SUMMARY

The general relationship between macroscopic and microscopic elasticity has been established for primitive crystals using a recently published microscopic formalism. The relationship is more useful and elegant than is possible if the Born-Huang microscopic approach is used. For example, the *n*th-order macroscopic elasticity coefficients involve only the *n*th order microscopic coefficients and the relationship between them is a direct one.

Because of some inconsistencies between the Born-Huang approach and the more recent approach, the question of rotational invariance in the former has been investigated. It has been shown that the existing rotational invariance conditions of the Born-Huang theory are not sufficient in general and additional requirements have been derived. These requirements are similar to, although somewhat less general than, those obtained independently by Gazis and Wallis.[12] When these are added to the existing Born-Huang approach, the inconsistencies vanish.

Finally, in order to demonstrate how the general macroscopic-microscopic relationship is used in practice, an illustrative study of the second and third order elasticity of the simple cubic structure has been carried out. These results show that the dominant contributions to some of the third-order elastic constants are from long-range (third-neighbor and more distant) interactions.

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[13] See, for example, P. B. Ghate, Phys. Rev. **139**, A1666 (1965) and references therein.

[14] See Table V of Ref. 12 and references therein.

[15] E. Bogardus, J. Appl. Phys. **36**, 2504 (1965).