Lattice Theory of Third-Order Elastic Constants of Nonprimitive, Nonpiezoelectric Lattices*

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Expressions for the third-order elastic constants of nonprimitive lattices are derived from lattice theory by the method of homogeneous deformation. The interlattice displacements are obtained as a power series in the strains from the condition that the strain energy is a minimum with respect to these displacements. For third-order elastic constants these displacements need to be known only to the first order in strain. The expressions for the elastic constants are verified by deriving the equation for wave propagation in a homogeneously strained crystal and comparing it with the equation from continuum mechanics. The expressions given here are valid only for nonpiezoelectric crystals.

I. INTRODUCTION

LATTICE–theoretical expressions for the third-order elastic constants of primitive lattices have been given by Leibfried and Ludwig.[1] Explicit expressions for the third-order elastic constants of the cubic primitive lattice in terms of the third-order coupling parameters have been derived by Coldwell-Horsefall.[2] In nonprimitive lattices, a macroscopic strain gives rise to interlattice displacements. This complicates the theoretical situation. In the alkali halides, each ion is at a position of a center of inversion. There can be no interlattice displacements in the alkali halides and the theoretical expressions in these crystals are similar to those for primitive lattices. The elastic constants of these crystals have been studied theoretically by Bross,[3] N'ran'yan,[4,5] and Ghate.[6]

Experimental data of the third-order elastic constants have recently become available for several materials occurring in nonprimitive lattice structures, such as[7,8] Si and Ge.[7,8,9,10] For an analysis and utilization of these data in terms of a force-constant model, the general relation between the third-order elastic constants and the third-order coupling parameters for nonprimitive lattices must be known.

In this paper, the general lattice-theoretical expressions for the third-order elastic constants of nonprimitive lattice are derived by the method of homogeneous deformation. The interlattice displacements are eliminated by imposing the condition that, for a given macroscopic strain, the energy must be a minimum with respect to these inner displacements. The inner displacements are obtained as a power series in the strain components. For the strain energy up to the third-order in strain, we need to know the inner displacements only up to the first-order in the strain. The expressions for the elastic constants are verified by the method of long waves. The equation for wave propagation in a homogeneously strained medium is derived from lattice theory. It is then compared with the equation of Thurston and Brugger[11] based on continuum theory. In this process we derive a Kun-Huang relation for third-order coupling parameters. This relation has already been given by Leibfried and Ludwig.[1]

Before proceeding to the derivations the notation used in the following pages is explained below:

L, M, N, upper case letters stand for cell indices.

λ, μ, ν, Greek letters stand for basis indices.

l, m, n, lower case letters refer to the Cartesian components.

$F_{jk,pm,rs}$, symmetric with respect to interchanges $(j\leftrightarrow k)$; $(p\leftrightarrow m)$; $(r\leftrightarrow s)\cdots$ and $(jk)\leftrightarrow(pm)$; $(pm)\leftrightarrow(rs)$, and $(rs)\leftrightarrow(jk)$.

$F_{[jk,pm]}$, symmetric with respect to interchanges $(j\leftrightarrow k)$; $(p\leftrightarrow m)$; but not with respect to $(jk)\leftrightarrow(pm)$.

$F_{jk,[rs],pm}$, symmetric with respect to $(j\leftrightarrow k)$; $(p\leftrightarrow m)$; but not with respect to $(r\leftrightarrow s)$.

$F_{j,(kp),(rs)}$, symmetric only with respect to $(kp)\leftrightarrow(rs)$.

$X_j(L\lambda)$, jth component of the position vector of atom $(L\lambda)$ in the unstrained state.

$u_j(L\lambda)$, jth component of the displacement of atom $(L\lambda)$ from the initial configuration.

$\Phi_{jkl}(L\lambda,M\mu,N\nu)=\partial^3\Phi/\partial u_j(L\lambda)\partial u_k(M\mu)\partial u_l(N\nu)$, Φ is the potential energy of the crystal.

v_a, volume of the unit cell in the undeformed state.

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II. METHOD OF HOMOGENEOUS DEFORMATION

We consider a crystal of large but finite volume V. The crystal is assumed to be free of any forces or stresses in the initial state. So

$$\Phi_j(L\lambda)=0$$

for every atom $(L\lambda)$. The potential energy of the crystal is expanded in powers of the atomic displacements $u_j(L\lambda)$:

$$\Phi=\Phi_0+\Phi_2+\Phi_3, \tag{1a}$$

where

$$\Phi_2=\tfrac{1}{2}\sum_{LM}\sum_{\lambda\mu}\sum_{jk}\Phi_{jk}(L\lambda,M\mu)u_j(L\lambda)u_k(M\mu), \tag{1b}$$

$$\Phi_3=\tfrac{1}{6}\sum_{LMN}\sum_{\lambda\mu\nu}\sum_{jkr}\Phi_{jkr}(L\lambda,M\mu,N\nu)\times u_j(L\lambda)u_k(M\mu)u_r(N\nu), \tag{1c}$$

The second-order crystal potential (CP) $\Phi_{jk}(L\lambda,M\mu)$ satisfy the following conditions[1]:

$$\Phi_{jk}(L\lambda,M\mu)=\Phi_{kj}(M\mu,L\lambda), \tag{2a}$$

$$\sum_{M\mu}\Phi_{jk}(L\lambda,M\mu)=\sum_{L\lambda}\Phi_{jk}(L\lambda,M\mu)=0 \tag{2b}$$

(translational invariance),

$$\sum_{M\mu}\Phi_{jk}(L\lambda,M\mu)X_l(M\mu)=\sum_{M\mu}\Phi_{jl}(L\lambda,M\mu)X_k(M\mu) \tag{2c}$$

(rotational invariance).

For an infinite lattice

$$\Phi_{jk}(L\lambda,M\mu)=\Phi_{jk}(0\lambda,\,M-L\mu)=\Phi_{jk}(L-M\lambda,\,0\mu). \tag{2d}$$

The conditions (2b) and (2c) become

$$\sum_{M\mu}\Phi_{jk}(0\lambda,M\mu)=0, \tag{2e}$$

$$\sum_{M\mu}\Phi_{jk}(0\lambda,M\mu)X_l(0\lambda,M\mu)=\sum_{M\mu}\Phi_{jl}(0\lambda,M\mu)X_k(0\lambda,M\mu), \tag{2f}$$

where

$$X_l(L\lambda,M\mu)=X_l(M\mu)-X_l(L\lambda).$$

The third-order CP's $\Phi_{jkr}(L\lambda,M\mu,N\nu)$ satisfy the following conditions[1]:

$$\Phi_{jkr}(L\lambda,M\mu,N\nu)=\Phi_{jrk}(L\lambda,N\nu,M\mu)=\Phi_{kjr}(M\mu,L\lambda,N\nu), \tag{3a}$$

$$\sum_{L\lambda}\Phi_{jkr}(L\lambda,M\mu,N\nu)=\sum_{M\mu}\Phi_{jkr}(L\lambda,M\mu,N\nu)=\sum_{N\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)=0 \tag{3b}$$

(translational invariance).

$$\sum_{N\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_s(N\nu)-\Phi_{js}(L\lambda,M\mu)\delta_{kr}-\Phi_{sk}(L\lambda,M\mu)\delta_{jr} \tag{3c}$$

must be symmetric in $(r\leftrightarrow s)$ (rotational invariance).

For an infinite lattice

$$\Phi_{jkr}(L\lambda,M\mu,N\nu)=\Phi_{jkr}(0\lambda,\,M-L\mu,\,N-L\nu), \tag{3d}$$

(3b) and (3c) are now written as

$$\sum_{M\mu}\Phi_{jkr}(0\lambda,M\mu,N\nu)=\sum_{N\nu}\Phi_{jkr}(0\lambda,M\mu,N\nu)=0, \tag{3e}$$

$$\sum_{N\nu}\Phi_{jkr}(0\lambda,M\mu,N\nu)X_s(0\lambda,N\nu)-\Phi_{js}(0\lambda,M\mu)\delta_{kr}-\Phi_{sk}(0\lambda,M\mu)\delta_{jr} \tag{3f}$$

must be symmetric in r and s.

For atoms within the body of the crystal we could expect (2d)–(2f) and (3d)–(3f) to be valid. For surface atoms this will not be so.

In a homogeneous deformation

$$u_j(L\lambda)=\sum_p\epsilon_{jp}X_p(L\lambda)+w_j(\lambda), \tag{4}$$

$\epsilon_{js}=(\partial X_j'/\partial X_s-\delta_{js})$ is the deformation parameter and $w_j(\lambda)$ is the jth component of the internal displacement of the sublattice λ. In order to express the strain energy in a form invariant with respect to rigid rotation the proper parameters to use are (Born and Huang[12])

$$\eta_{ij}=\tfrac{1}{2}[\epsilon_{ij}+\epsilon_{ji}+\sum_p\epsilon_{pi}\epsilon_{pj}], \tag{5a}$$

$$\bar{w}_j(\lambda)=w_j(\lambda)+\sum_p\epsilon_{pj}w_p(\lambda). \tag{5b}$$

After substituting for $u_j(L\lambda)$ from (4), (1b) can be written as

$$\Phi_2=\tfrac{1}{2}\sum_{jk}\sum_{LM}\sum_{\lambda\mu}\Phi_{jk}(L\lambda,M\mu)w_j(\lambda)w_k(\mu) \tag{6a}$$

$$+\sum_{jkm}\sum_{LM}\sum_{\lambda\mu}\Phi_{jk}(L\lambda,M\mu)\times X_m(M\mu)w_j(\lambda)\epsilon_{km} \tag{6b}$$

$$+\tfrac{1}{2}\sum_{jkpm}\sum_{LM}\sum_{\lambda\mu}\Phi_{jk}(L\lambda,M\mu)\times X_p(L\lambda)X_m(M\mu)\epsilon_{jp}\epsilon_{km}. \tag{6c}$$

In the expressions (6a), (6b), and (6c), the following lattice sums can be defined:

$$[\lambda j,\mu k]=\frac{1}{V}\sum_{LM}\Phi_{jk}(L\lambda,M\mu)=[\mu k,\lambda j], \tag{7a}$$

$$(\lambda j,km)=\frac{1}{V}\sum_{LM}\sum_{\mu}\Phi_{jk}(L\lambda,M\mu)X_m(M\mu)$$

$$=\frac{1}{V}\sum_{LM}\sum_{\mu}\Phi_{jk}(L\lambda,M\mu)X_m(L\lambda,M\mu), \tag{7b}$$

$$c_{jp,km}=\frac{1}{V}\sum_{LM}\sum_{\lambda\mu}\Phi_{jk}(L\lambda,M\mu)\times X_p(L\lambda)X_m(M\mu). \tag{7c}$$

$(\lambda j,km)$ is symmetric in k and m and $c_{jp,km}$ is symmetric with respect to $(j\leftrightarrow p)$, $(k\leftrightarrow m)$, and $(jp)\leftrightarrow(km)$.

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[12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1962), Chap. VI.

This can be shown with the help of (2c). The contribution of the surface atoms to the sum (7a) becomes negligible ($\sim V^{-1/3}$) compared to the contribution from the atoms in the body of the crystal for large volumes. This will not be the case when the lattice sum involves the position coordinates $X_j(M\mu)$. Following Leibfried and Ludwig,[1] we can define new lattice sums by replacing the position coordinates with the relative coordinates $X_j(L\lambda,M\mu)$. By doing so, we make the contributions from the surface atoms negligible compared to the contributions from the volume atoms. Replacement of $X_m(M\mu)$ by $X_m(L\lambda,M\mu)$ in (7b) does not give rise to a new lattice sum because of (2b). Making use of (2d) for the atoms within the volume of the crystal, we can write (7a) and (7b) as

$$[\lambda j,\mu k]=\frac{1}{v_a}\sum_M \Phi_{jk}(0\lambda,M\mu)\,, \tag{7a'}$$

$$(\lambda j,km)=\frac{1}{v_a}\sum_M \sum_\mu \Phi_{jk}(0\lambda,M\mu)X_m(0\lambda,M\mu)\,. \tag{7b'}$$

v_a is the volume of the unit cell in the undeformed crystal. Instead of (7c) we define a new lattice sum

$$\begin{aligned}\hat{c}_{[jk,pm]}&=-\frac{1}{2V}\sum_{LM}\sum_{\lambda\mu}\Phi_{jk}(L\lambda,M\mu)\\ &\qquad\times X_p(L\lambda,M\mu)X_m(L\lambda,M\mu)\\ &=-\frac{1}{2v_a}\sum_M\sum_{\lambda\mu}\Phi_{jk}(0\lambda,M\mu)\\ &\qquad\times X_p(0\lambda,M\mu)X_m(0\lambda,M\mu)\,.\end{aligned} \tag{8}$$

From (7c) and (8) it follows that

$$2\hat{c}_{[jk,pm]}=c_{jp,km}+c_{jm,kp}\,. \tag{9}$$

So

$$\hat{c}_{[jk,pm]}=\hat{c}_{jk,pm}\,, \tag{10}$$

i.e., $\hat{c}_{[jk,pm]}$ must also be symmetric in $(jk)\leftrightarrow(pm)$.

This is the Kun-Huang relation on the second-order coupling parameters for an infinite lattice initially free of stress. This cannot be derived from the rotational invariance relation for an infinite lattice. So this represents new conditions on the second-order coupling parameters. In terms of the $\hat{c}_{jk,pm}$, the $c_{jk,pm}$ are given by

$$c_{jp,km}=\hat{c}_{jk,pm}+\hat{c}_{kp,jm}-\hat{c}_{jp,km}\,. \tag{11}$$

Making use of (5a) and (5b) and (7a)–(7b′) we can write Φ_2 as

$$\Phi_2=\Phi_2'+\Phi_2''\,,$$

$$\Phi_2'=V\{\tfrac{1}{2}\sum_{\lambda\mu}\sum_{jk}[\lambda j,\mu k]\bar{w}_j(\lambda)\bar{w}_k(\mu)+\sum_\lambda\sum_{jkm}(\lambda j,km)\bar{w}_j(\lambda)\eta_{km}+\tfrac{1}{2}\sum_{jkpm}c_{jp,km}\eta_{jp}\eta_{km}\}\,, \tag{12a}$$

$$\Phi_2''=-V\sum_{\lambda\mu}\sum_{jkp}[\lambda j,\mu k]w_k(\lambda)w_p(\mu)\epsilon_{pj} \tag{12b}$$

$$-V\times\tfrac{1}{2}\sum_\lambda\sum_{jkmp}(\lambda j,km)[w_j(\lambda)\epsilon_{pk}\epsilon_{pm}+w_p(\lambda)\epsilon_{pj}(\epsilon_{km}+\epsilon_{mk})] \tag{12c}$$

$$-V\times\tfrac{1}{2}\sum_{jpkmr}c_{jp,km}\epsilon_{jp}\epsilon_{rk}\epsilon_{rm}\,. \tag{12d}$$

Φ_2'' must be added on to the corresponding terms from Φ_3. Substituting for $u_j(L\lambda)$ from (4) in (1c) we get

$$\Phi_3=\tfrac{1}{6}\sum_{jkr}\sum_{LMN}\sum_{\lambda\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)w_j(\lambda)w_k(\mu)w_r(\nu) \tag{13a}$$

$$+\tfrac{1}{2}\sum_{jkrs}\sum_{LMN}\sum_{\lambda\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_s(N\nu)w_j(\lambda)w_k(\mu)\epsilon_{rs} \tag{13b}$$

$$+\tfrac{1}{2}\sum_{jkrms}\sum_{LMN}\sum_{\lambda\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_m(M\mu)X_s(N\nu)w_j(\lambda)\epsilon_{km}\epsilon_{rs} \tag{13c}$$

$$+\tfrac{1}{6}\sum_{jkpmrs}\sum_{LMN}\sum_{\lambda\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_p(L\lambda)X_m(M\mu)X_s(N\nu)\epsilon_{jp}\epsilon_{km}\epsilon_{rs}\,. \tag{13d}$$

Adding Φ_2'' to Φ_3 we can write

$$\Phi_2''+\Phi_3=\frac{V}{6}\sum_{jkr}\sum_{\lambda\mu\nu}\sum_{LMN}\Phi_{jkr}(L\lambda,M\mu,N\nu)w_j(\lambda)w_k(\mu)w_r(\nu) \tag{13a'}$$

$$+\tfrac{1}{2}V\sum_{jkrs}\sum_{\lambda\mu}\left[\frac{1}{V}\sum_{LMN}\sum_\nu\Phi_{jkr}(L\lambda,M\mu,N\nu)X_s(N\nu)-[\lambda j,\mu s]\delta_{rk}-[\lambda s,\mu k]\delta_{rj}\right]w_j(\lambda)w_k(\mu)\epsilon_{rs} \tag{13b'}$$

$$+\tfrac{1}{2}V\sum_{jkmrs}\sum_\lambda\left[\frac{1}{V}\sum_{LMN}\sum_{\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_m(M\mu)X_s(N\nu)-(\lambda m,rs)\delta_{jk}-(\lambda j,ms)\delta_{kr}\right]w_j(\lambda)\epsilon_{km}\epsilon_{rs} \tag{13c'}$$

$$+\tfrac{1}{6}V\sum_{jpkmrs}\left[\frac{1}{V}\sum_{LMN}\sum_{\lambda\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_p(L\lambda)X_m(M\mu)X_s(N\nu)-c_{pm,rs}\delta_{jk}-c_{km,ps}\delta_{jr}-c_{jp,ms}\delta_{kr}\right]\epsilon_{jp}\epsilon_{km}\epsilon_{rs}\,. \tag{13d'}$$

We can now define the following lattice sums

$$[\lambda j,\mu k,\nu r]=\frac{1}{V}\sum_{LMN}\Phi_{jkr}(L\lambda,M\mu,N\nu)=\frac{1}{v_a}\sum_{MN}\Phi_{jkr}(0\lambda,M\mu,N\nu)\,, \tag{14a}$$

$$[\lambda j,\mu k,rs]=\frac{1}{V}\sum_{LMN}\sum_{\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_s(N\nu)-[\lambda j,\mu s]\delta_{rk}-[\lambda s,\mu k]\delta_{rj}\,, \tag{14b}$$

$$[\lambda j,km,rs]=\frac{1}{V}\sum_{LMN}\sum_{\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_m(M\mu)X_s(N\nu)-(\lambda s,mk)\delta_{jr}-(\lambda m,rs)\delta_{jk}-(\lambda j,ms)\delta_{kr}\,, \tag{14c}$$

$$c_{jp,km,rs}=\frac{1}{V}\sum_{LMN}\sum_{\lambda\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_p(L\lambda)X_m(M\mu)X_s(N\nu)-c_{pm,rs}\delta_{jk}-c_{km,ps}\delta_{jr}-c_{jp,ms}\delta_{kr}\,. \tag{14d}$$

With the help of (7a′) and (3c) we can show that $[\lambda j,\mu k,rs]$ is symmetric with respect to $(r\leftrightarrow s)$. $X_s(N\nu)$ can be replaced with $X_s(0\lambda,N\nu)$ without altering the lattice sum in (13b′). At the same time the contribution from the surface atoms becomes negligible compared to the volume contribution. We can make use of (3d) for third-order coupling parameters for atoms in the body of the crystal. (14b) can be written as

$$[\lambda j,\mu k,rs]=\frac{1}{v_a}\sum_{MN}\sum_{\nu}\Phi_{jkr}(0\lambda,M\mu,N\nu)X_s(0\lambda,N\nu)-[\lambda j,\mu s]\delta_{rk}-[\lambda s,\mu k]\delta_{rj}\,. \tag{14b′}$$

With the help of (7b′) and (3c), it can be shown that $[\lambda j,km,rs]$ is symmetric in $(r\leftrightarrow s)$. From the definition (14c) it is obvious that $[\lambda j,km,rs]$ is symmetric with respect to $(km)\leftrightarrow(rs)$. So it is also symmetric in $(k\leftrightarrow m)$. We can replace $X_m(M\mu)$ and $X_s(N\nu)$ with $X_m(0\lambda,M\mu)$ and $X_s(0\lambda,N\nu)$ without altering the sum (14c). So we could write $[\lambda j,km,rs]$ as

$$[\lambda j,km,rs]=[\lambda j,(km),(rs)]-(\lambda s,km)\delta_{jr}-(\lambda m,rs)\delta_{jk}-(\lambda j,ms)\delta_{kr}\,, \tag{14c′}$$

$$[\lambda j,(km),(rs)]=\frac{1}{v_a}\sum_{MN}\sum_{\mu\nu}\Phi_{jkr}(0\lambda,M\mu,N\nu)X_m(0\lambda,M\mu)X_s(0\lambda,N\nu)\,. \tag{14d′}$$

$c_{jp,km,rs}$ defined in (14d) is obviously symmetric in $(jp)\leftrightarrow(km)\leftrightarrow(rs)$. It is also symmetric in $(r\leftrightarrow s)$ and hence $(k\leftrightarrow m)$ and $(j\leftrightarrow p)$. This can be shown with the help of (7c) and (3c). To avoid the surface contribution, we define a new lattice sum

$$\begin{aligned}\hat{c}_{jk,[rs],pm}&=-\frac{1}{2V}\sum_{LMN}\sum_{\lambda\mu\nu}\Phi_{jkr}(L\lambda,M\mu,N\nu)X_p(L\lambda,M\mu)X_m(L\lambda,M\mu)X_s(L\lambda,N\nu)\\&=-\frac{1}{2v_a}\sum_{\lambda\mu\nu}\sum_{MN}\Phi_{jkr}(0\lambda,M\mu,N\nu)X_p(0\lambda,M\mu)X_m(0\lambda,M\mu)X_s(0\lambda,N\nu)\,.\end{aligned} \tag{15}$$

From (15), (14d), and (8) it follows that

$$2[\hat{c}_{jk,[rs],pm}-\hat{c}_{[js,pm]}\delta_{kr}-\hat{c}_{[sk,pm]}\delta_{jr}]=c_{jp,km,rs}+c_{jm,kp,rs}+(c_{pm,rs}+c_{mp,rs})\delta_{jk}\,. \tag{16}$$

Now

$$\hat{c}_{jk,[rs],pm}-\hat{c}_{[js,pm]}\delta_{kr}-\hat{c}_{[sk,pm]}\delta_{jr}$$

is symmetric in r and s. This can be seen from (15), (8), and (3f). In addition to the above symmetry,

$$\hat{c}_{jk,[rs],pm}-\hat{c}_{[js,pm]}\delta_{kr}-\hat{c}_{[sk,pm]}\delta_{jr}-c_{pm,rs}\delta_{jk}$$

must be symmetric in the interchange $(jp)\leftrightarrow(km)$. This is the Kun-Huang relation on third-order coupling parameters derived by Leibfried and Ludwig.[1] It may impose additional restrictions on the third-order coupling parameters. We can derive an expression for $c_{jp,km,rs}$ from Eq. (16). We add to (16) the equation obtained by interchanging j with p and subtract the equation resulting from the interchange of p with k. Then

$$\begin{aligned}c_{jp,km,rs}=\hat{c}_{jk,[rs],pm}&+\hat{c}_{pk,[rs],jm}-\hat{c}_{jp,[rs],km}\\&-[\hat{c}_{[sk,pm]}-\hat{c}_{[sp,km]}]\delta_{jr}\\&-[\hat{c}_{[js,pm]}+\hat{c}_{[ps,jm]}]\delta_{kr}\\&-[\hat{c}_{[sk,jm]}-\hat{c}_{[js,km]}]\delta_{pr}\\&-[c_{pm,rs}\delta_{jk}+c_{jm,rs}\delta_{kp}-c_{km,rs}\delta_{jp}]\,.\end{aligned} \tag{17}$$

Making use of the symmetries of the lattice sums (14a)–(14d), we can write $\Phi_2''+\Phi_3$ as follows. As we are

interested in the energy only up to the third-order in the strains, we can write $\bar{w}$ for w and η_{rs} for $\frac{1}{2}(\epsilon_{rs}+\epsilon_{sr})$ in these terms. So

$$\begin{aligned}\Phi_2''+\Phi_3=&\tfrac{1}{6}V\sum_{abc}\sum_{\lambda\mu\nu}[\lambda a,\mu b,\nu c]\bar{w}_a(\lambda)\bar{w}_b(\mu)\bar{w}_c(\nu)\\&+\tfrac{1}{2}V\sum_{jkrs}\sum_{\lambda\mu}[\lambda j,\mu k,rs]\bar{w}_j(\lambda)\bar{w}_k(\mu)\eta_{rs}\\&+\tfrac{1}{2}V\sum_{jkmrs}\sum_{\lambda}[\lambda j,km,rs]\bar{w}_j(\lambda)\eta_{km}\eta_{rs}\\&+\tfrac{1}{6}V\sum_{jpkmrs}c_{jp,km,rs}\eta_{jp}\eta_{km}\eta_{rs}.\end{aligned}\tag{18}$$

So the strain energy per unit volume of the undeformed crystal is

$$\begin{aligned}\varphi=\frac{1}{V}[\Phi_2+\Phi_3]=&\tfrac{1}{2}\sum_{\lambda\mu}\sum_{jk}[\lambda j,\mu k]\bar{w}_j(\lambda)\bar{w}_k(\mu)\\&+\sum_{\lambda}\sum_{jkm}(\lambda j,km)\bar{w}_j(\lambda)\eta_{km}+\tfrac{1}{2}\sum_{jpkm}c_{jp,km}\eta_{jp}\eta_{km}\\&+\tfrac{1}{6}\sum_{jkr}\sum_{\lambda\mu\nu}[\lambda j,\mu k,\nu r]\bar{w}_j(\lambda)\bar{w}_k(\mu)\bar{w}_r(\nu)\\&+\tfrac{1}{2}\sum_{jkrs}\sum_{\lambda\mu}[\lambda j,\mu k,rs]\bar{w}_j(\lambda)\bar{w}_k(\mu)\eta_{rs}\\&+\tfrac{1}{2}\sum_{jkmrs}\sum_{\lambda}[\lambda j,km,rs]\bar{w}_j(\lambda)\eta_{km}\eta_{rs}\\&+\tfrac{1}{6}\sum_{jpkmrs}c_{jp,km,rs}\eta_{jp}\eta_{km}\eta_{rs}.\end{aligned}\tag{19}$$

The components $\bar{w}_j(\lambda)$ are eliminated by imposing the condition that

$$\partial\varphi/\partial\bar{w}_j(\lambda)=0.$$

This leads to the equation

$$\begin{aligned}&\sum_{\mu}\sum_{k}[\lambda j,\mu k]\bar{w}_k(\mu)\\&\quad=-\sum_{km}(\lambda j,km)\eta_{km}\\&\qquad-\sum_{\mu\nu}\sum_{kl}[\lambda j,\mu k,\nu l](1-\tfrac{1}{2}\delta_{\mu\nu}\delta_{kl})\bar{w}_k(\mu)\bar{w}_l(\nu)\\&\qquad-\sum_{\mu}\sum_{krs}[\lambda j,\mu k,rs]\bar{w}_k(\mu)\eta_{rs}\\&\qquad-\tfrac{1}{2}\sum_{kmrs}[\lambda j,km,rs]\eta_{km}\eta_{rs}.\end{aligned}\tag{20}$$

This equation can be solved to yield $\bar{w}_j(\lambda)$ in a power series in the strain. As long as we are interested in the energy up to the third order in the strains, we need to know $\bar{w}_j(\lambda)$ only up to the second order in the strains. Writing $\bar{w}_j(\lambda)=\bar{w}_j^{(1)}(\lambda)+\bar{w}_j^{(2)}(\lambda)$, $\bar{w}_j^{(1)}(\lambda)$ is the solution of the equation

$$\sum_{\mu}\sum_{k}[\lambda j,\mu k]\bar{w}_k(\mu)=-\sum_{km}(\lambda j,km)\eta_{km}.\tag{21}$$

The Det$[\lambda j,\mu k]$ is singular because $\sum_{\lambda}[\lambda j,\mu k]=0$. However, we can assume the sublattice $\lambda=1$ to have no internal displacement, i.e., $\bar{w}_j(1)=0$ and calculate the relative displacement of the other sublattices. Following the procedure of Born and Huang,[13] we take the $(3n-3)\times(3n-3)$ submatrix $\Gamma^0(3n-3)$ of $[\lambda j,\mu k]$ by omitting the 3 rows and 3 columns $\lambda=1$ or $\mu=1$. The inverse is then bordered with zeros to make a $3n\times 3n$ matrix $\{\lambda j,\mu k\}$. We can then write the solution as

$$\bar{w}_j^{(1)}(\lambda)=-\sum_{km}A(\lambda j,km)\eta_{km},\tag{22}$$

where

$$A(\lambda j,km)=\sum_{\mu}\sum_{l}\{\lambda j,\mu l\}(\mu l,km).\tag{23}$$

Substituting for $\bar{w}_j(\lambda)$ in terms of $\bar{w}_j^{(1)}(\lambda)+\bar{w}_j^{(2)}(\lambda)$ the strain energy (19) can be written as

$$\begin{aligned}\varphi=&\tfrac{1}{2}\sum_{\lambda\mu}\sum_{jk}[\lambda j,\mu k]\bar{w}_j^{(1)}(\lambda)\bar{w}_k^{(1)}(\mu)+\sum_{\lambda\mu}\sum_{jk}[\lambda j,\mu k]\bar{w}_k^{(1)}(\mu)\bar{w}_j^{(2)}(\lambda)\\&+\sum_{\lambda}\sum_{jkm}(\lambda j,km)\bar{w}_j^{(1)}(\lambda)\eta_{km}+\sum_{\lambda}\sum_{jkm}(\lambda j,km)\bar{w}_j^{(2)}(\lambda)\eta_{km}+\tfrac{1}{2}\sum_{jpkm}c_{jp,km}\eta_{jp}\eta_{km}\\&+\tfrac{1}{6}\sum_{jkr}\sum_{\lambda\mu\nu}[\lambda j,\mu k,\nu r]\bar{w}_j^{(1)}(\lambda)\bar{w}_k^{(1)}(\mu)\bar{w}_r^{(1)}(\nu)+\tfrac{1}{2}\sum_{jkrs}\sum_{\lambda\mu}[\lambda j,\mu k,rs]\bar{w}_j^{(1)}(\lambda)\bar{w}_k^{(1)}(\mu)\eta_{rs}\\&+\tfrac{1}{2}\sum_{jkmrs}\sum_{\lambda}[\lambda j,km,rs]\bar{w}_j^{(1)}(\lambda)\eta_{km}\eta_{rs}+\tfrac{1}{6}\sum_{jkpmrs}c_{jp,km,rs}\eta_{jp}\eta_{km}\eta_{rs}.\end{aligned}\tag{24}$$

Because of (21), the terms in $\bar{w}_j^{(2)}(\lambda)$ cancel out. So to get φ correct to third order in strains it is enough to know $\bar{w}$ to the first order in strains. Finally, substituting for $\bar{w}_j^{(1)}(\lambda)$ from (22) we can write (24) as

$$\varphi=\tfrac{1}{2}\sum_{jp,km}\bar{c}_{jp,km}\eta_{jp}\eta_{km}+\tfrac{1}{6}\sum_{jpkmrs}\bar{c}_{jpkmrs}\eta_{jp}\eta_{km}\eta_{rs},\tag{25}$$

where

$$\bar{c}_{jp,km}=c_{jp,km}-\sum_{\nu}\sum_{l}(\nu l,jp)A(\nu l,km),\tag{26}$$

$$\begin{aligned}\bar{c}_{jp,km,rs}=&c_{jp,km,rs}-\sum_{\nu}\sum_{l}[E(\nu l,[km,rs])A(\nu l,jp)+E(\nu l,[rs,jp])A(\nu l,km)+E(\nu l,[jp,km])A(\nu l,rs)]\\&-\sum_{\lambda\mu\nu}\sum_{abc}[\lambda a,\mu b,\nu c]A(\lambda a,jp)A(\mu b,km)A(\nu c,rs).\end{aligned}\tag{27}$$

$\bar{c}_{jp,km}$ and $\bar{c}_{jp,km,rs}$ are the second- and third-order macroscopic elastic constants

$$E(\nu l,[km,rs])=[\nu l,km,rs]-c(\nu l,[km,rs]),\tag{28a}$$

$$c(\nu l,[km,rs])=\sum_{\alpha}\sum_{a}[\nu l,\alpha a,rs]A(\alpha a,km).\tag{28b}$$

When every atom is at a center of inversion the sums $(\lambda j,km)$, $A(\lambda j,km)$, $(\lambda j,km,rs)$ are zero. There can be no internal displacement and

$$\bar{c}_{jp,km}=c_{jp,km};\quad \bar{c}_{jp,km,rs}=c_{jp,km,rs}.$$

The above expressions are valid for the alkali halides.

The expressions (26) and (27) are valid only for non-piezoelectric crystals. In a piezoelectric crystal, a macroscopic strain gives rise to a macroscopic electric field which depends on the shape of the specimen. Then we have to separate out from the strain-energy expression (19) the contribution due to the macroscopic electric field. This problem is under investigation.

[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1962), p. 234.

III. LONG-WAVE METHOD

Thurston and Brugger[11] have given the following equation from macroscopic elasticity theory for wave propagation in a homogeneously strained crystal[14]:

$$\rho_0 W^2 s_j = \sum_{kpm} A_{(jp),(km)} N_p N_m s_k . \tag{29}$$

Here ρ_0 is the density of the crystal in the undeformed state, W is the "natural" velocity of propagation normal to a plane of natural normal $\mathbf{N}$ and s_j is the jth component of the displacement from the homogeneously strained state. Using a strain-energy expression of the form (25) and the expression for $A_{(jp),(km)}$ given by Thurston and Brugger, we can write

$$A_{(jp),(km)} = \bar{c}_{pj,mk} + \sum_{rs} [\bar{c}_{pj,mk,rs} + \bar{c}_{pm,rs}\delta_{jk}]\eta_{rs} + \sum_q \bar{c}_{pq,mk}\epsilon_{jq} + \sum_q \bar{c}_{pj,mq}\epsilon_{kq} . \tag{30}$$

When the strain energy is known up to third order in the deformation, $A_{(jp),(km)}$ is known only to the first order in the deformation. In (30) η_{rs} can be replaced by $\frac{1}{2}(\epsilon_{rs}+\epsilon_{sr})$.

In the long-wave method, we derive from lattice theory the equation for wave propagation in a indefinitely extended medium. This equation is compared with (29) and (30) and the expression for the elastic constants are derived.

We consider a homogeneously deformed lattice. The atomic displacements $u_j(L\lambda)$ are given by (4). The atoms are given a further infinitesmal displacement $s_j(L\lambda)$ from the deformed state. The equations of motion can be shown to be

$$M(\lambda)\ddot{s}_j(L\lambda) = -\sum_M \sum_\mu \sum_k \Psi_{jk}(L\lambda,M\mu)s_k(M\mu) . \tag{31}$$

$M(\lambda)$ is the mass of the λ-type atom.

$$\Psi_{jk}(L\lambda,M\mu) = \Phi_{jk}(L\lambda,M\mu) + \Delta_{jk}(L\lambda,M\mu) , \tag{32a}$$

$$\Delta_{jk}(L\lambda,M\mu) = \sum_N \sum_\nu \sum_l \Phi_{jkl}(L\lambda,M\mu,N\nu)u_l(N\nu) . \tag{32b}$$

If we seek a solution of (31) in the form

$$s_j(L\lambda) = s_j(\lambda)\exp i[\omega t - Y\mathbf{N}\cdot\mathbf{X}(L\lambda)]$$

[this equation is of the same form as Eq. (3.9) of Thurston and Brugger[11]],

$$M(\lambda)\omega^2 s_j(\lambda) = \sum_M \sum_\mu \sum_k \Psi_{jk}(L\lambda,M\mu) \times (\exp\{-[iY\mathbf{N}\cdot\mathbf{X}(L\lambda,M\mu)]\})s_k(\mu) . \tag{33}$$

Here the "wave number" of the wave is Y and we are considering a wave traveling normal to a plane whose natural normal is $\mathbf{N}$. $\omega^2/Y^2 = W^2$ when Y is small.

The long-wave method developed by Born and Huang[15] can be applied to Eq. (33) to obtain the equation in the form

$$\rho_0 W^2 s_j{}^0 = \sum_{kpm} s_k{}^0 N_p N_m \Big[-\frac{1}{2v_a}\sum_M \sum_{\lambda\mu} \Psi_{jk}(0\lambda,M\mu)X_p(0\lambda,M\mu)X_m(0\lambda,M\mu) + \frac{1}{v_a}\sum_{MP}\sum_{\lambda\mu\sigma\pi}\sum_{qr}\Psi_{jq}(0\lambda,m\mu)X_p(0\lambda,M\mu)\Gamma^{-1}(\mu q,\sigma r)\Psi_{rk}(0\sigma,P\pi)X_m(0\sigma,P\pi)\Big] . \tag{34}$$

The matrix $\Gamma^{-1}(\mu q,\sigma r)$ is obtained as follows. $A(3n-3)\times(3n-3)$ matrix is obtained from $\sum_M \Psi_{jk}(0\lambda,M\mu)$ by omitting the 3 rows and 3 columns with $\lambda=1$ or $\mu=1$. The matrix is inverted. The inverse matrix bordered with zeros gives $\Gamma^{-1}(\mu q,\sigma r)$.

Comparing (34) with (29) the lattice-theoretical expression of $A_{(jp),(km)}$ can be written

$$A_{(jp),(km)} = -\frac{1}{2v_a}\sum_M \sum_{\lambda\mu} \Psi_{jk}(0\lambda,M\mu)X_p(0\lambda,M\mu)X_m(0\lambda,M\mu) \tag{35a}$$

$$+\frac{1}{v_a}\sum_{MP}\sum_{\lambda\mu\sigma\pi}\sum_{qr}\Psi_{jq}(0\lambda,M\mu)X_p(0\lambda,M\mu)\Gamma^{-1}(\mu q,\sigma r)\Psi_{rk}(0\sigma,P\pi)X_m(0\sigma,P\pi) . \tag{35b}$$

Substituting for $\Psi_{jk}(0\lambda,M\mu)$ and $u_j(L\lambda)$ from (32a), (32b), and (4) in (35a) yields

$$-\frac{1}{2v_a}\sum_M \sum_{\lambda\mu} \Phi_{jk}(0\lambda,M\mu)X_p(0\lambda,M\mu)X_m(0\lambda,M\mu) \tag{36a}$$

$$-\frac{1}{2v_a}\sum_{MN}\sum_{\lambda\mu\nu}\sum_{rs}\Phi_{jkr}(0\lambda,M\mu,N\nu)X_p(0\lambda,M\mu)X_m(0\lambda,M\mu)X_s(N\nu)\epsilon_{rs} \tag{36b}$$

$$-\frac{1}{2v_a}\sum_{MN}\sum_{\lambda\mu\nu}\sum_{r}\Phi_{jkr}(0\lambda,M\mu,N\nu)X_p(0\lambda,M\mu)X_m(0\lambda,M\mu)w_r(\nu) . \tag{36c}$$

[14] $A_{(jp),(km)}$ corresponds to $A^S{}_{jkpm}$ in Thurston and Brugger, Ref. 11.
[15] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1962), Chap. V.

(36a) and (36b) are the lattice sums $\hat{c}_{[jk,pm]}$ and $\sum_{rs}\hat{c}_{jk,[rs],pm}\epsilon_{rs}$ defined in (8) and (15), respectively. Making use of (3d), (3a), (3e), (36c) can be written as

$$\sum_\nu \sum_r [\nu r,[jk,pm]]w_r(\nu), \tag{37a}$$

where

$$[\nu r,[jk,pm]]=-\frac{1}{2v_a}\sum_{LM}\sum_{\lambda\mu}\Phi_{rjk}(0\nu,M\mu,L\lambda)X_p(M\mu,L\lambda)X_m(M\mu,L\lambda). \tag{37b}$$

Since $A_{(jp),(km)}$ is required only to the first order in the deformation, we can replace $w_r(\nu)$ with $\bar{w}_r^{(1)}(\nu)$ given by (22) and write (37a) as

$$-\sum_{rs}\sum_\nu\sum_l A(\nu l,rs)[\nu l,[jk,pm]]\eta_{rs}. \tag{38}$$

Now we evaluate (35b)

$$\sum_S \Psi_{qr}(0\mu,S\sigma)=v_a[\mu q,\sigma r]+D(\mu q,\sigma r), \tag{39a}$$

where

$$D(\mu q,\sigma r)=\sum_{ST}\sum_\tau\sum_s \Phi_{qrs}(0\mu,S\sigma,T\tau)u_s(T,\tau). \tag{39b}$$

$\Gamma^{-1}(\mu q,\sigma r)$ can be expanded in powers of $D(\mu q,\sigma r)$ and only terms up to the first power in $D(\mu q,\sigma r)$ need be retained.

$$\Gamma^{-1}(\mu q,\sigma r)=\frac{1}{v_a}\{\mu q,\sigma r\}-\frac{1}{v_a^2}\sum_{a\beta}\sum_{ab}\{\mu q,\alpha a\}D(\alpha a,\beta b)\{\beta b,\sigma r\}. \tag{40}$$

Substituting for $\Gamma^{-1}(\mu q,\sigma r)$, (35b) can be written up to the first power in displacement as

$$\frac{1}{v_a^2}\sum_{MP}\sum_{\lambda\mu\sigma\pi}\sum_{qr}\Phi_{jq}(0\lambda,M\mu)X_p(0\lambda,M\mu)\{\mu q,\sigma r\}\Phi_{rk}(0\sigma,P\pi)X_m(0\sigma,P\pi) \tag{41a}$$

$$+\frac{1}{v_a^2}\sum_{MP}\sum_{\lambda\mu\sigma\pi}\sum_{qt}\Phi_{jq}(0\lambda,M\mu)X_p(0\lambda,M\mu)\{\mu q,\sigma t\}\Delta_{tk}(0\sigma,P\pi)X_m(0\sigma,P\pi) \tag{41b}$$

$$+\frac{1}{v_a^2}\sum_{MP}\sum_{\lambda\mu\sigma\pi}\sum_{qt}\Delta_{jq}(0\lambda,M\mu)X_p(0\lambda,M\mu)\{\mu q,\sigma t\}\Phi_{tk}(0\sigma,P\pi)X_m(0\sigma,P\pi) \tag{41c}$$

$$-\frac{1}{v_a^3}\sum_{MP}\sum_{\lambda\mu\sigma\pi\alpha\beta}\sum_{qrab}\Phi_{jq}(0\lambda,M\mu)X_p(0\lambda,M\mu)\{\mu q,\alpha a\}D(\alpha a,\beta b)\{\beta b,\sigma r\}\Phi_{rk}(0\sigma,P\pi)X_m(0\sigma,P\pi). \tag{41d}$$

Using (2a), (2d), (7b′), and (23), (41a) can be written as

$$-\sum_\mu\sum_q(\mu q,jp)A(\mu q,km). \tag{41a′}$$

Substituting for $\Delta_{tk}(0\sigma,P\pi)$ from (32b), $u_j(L\lambda)$ from (4), and using (7b′), (41b) can be written as

$$-\frac{1}{v_a}\sum_{PN}\sum_{\mu\sigma\pi\nu}\sum_{qtl}(\mu q,jp)\Phi_{tkl}(0\sigma,P\pi,N\nu)w_l(\nu)X_m(0\sigma,P\pi)\{\mu q,\sigma t\} \tag{42a}$$

$$-\frac{1}{v_a}\sum_{PS}\sum_{\mu\sigma\pi\nu}\sum_{qlrs}(\mu q,jp)\{\mu q,\nu l\}\Phi_{lkr}(0\nu,P\pi,S\sigma)X_s(0\nu,S\sigma)X_m(0\nu,P\pi)\epsilon_{rs}. \tag{42b}$$

From (23) and (14b′) and replacing $w_l(\nu)$ with $\bar{w}_l^{(1)}(\nu)$ from (22), (42a) becomes

$$\sum_{\sigma\nu}\sum_{lrst}A(\sigma t,jp)A(\nu l,rs)\{[\sigma t,\nu l,km]+[\sigma m,\nu l]\delta_{tk}+[\sigma t,\nu m]\delta_{lk}\}\eta_{rs}. \tag{43}$$

Using (28b) this can be written as

$$\sum_\nu\sum_{lrs}\{c(\nu l,[jp,km])A(\nu l,rs)+A(\nu k,jp)(\nu l,rs)\delta_{lm}+A(\nu k,rs)(\nu l,jp)\delta_{lm}\}\eta_{rs}. \tag{44}$$

(42b) can be rewritten with the help of (14d′) and (23) as

$$-\sum_\nu\sum_{lrs}A(\nu l,jp)[\nu l,(km),(rs)]\epsilon_{rs}. \tag{45}$$

From (41c) we get two terms similar to (44) and (45), namely

$$\sum_\nu\sum_{lrs}\{c(\nu l,[km,jp])A(\nu l,rs)+A(\nu j,km)(\nu l,rs)\delta_{lp}+A(\nu j,rs)(\nu l,km)\delta_{lp}\}\eta_{rs} \tag{46}$$

and

$$-\sum_\nu\sum_{lrs}A(\nu l,km)[\nu l,(jp),(rs)]\epsilon_{rs}. \tag{47}$$

With the help of (2a), (2d), (7b′), and (23), (41d) can be simplified to

$$(1/v_a)\sum_{\alpha\beta}\sum_{ab}A(\alpha a,jp)D(\alpha a,\beta b)A(\beta b,km)\,. \tag{48}$$

Substituting for $D(\alpha a,\beta b)$ from (39b), (48) becomes

$$(1/v_a)\sum_{BP}\sum_{\alpha\beta\pi}\sum_{abc}A(\alpha a,jp)\Phi_{abc}(0\alpha,B\beta,P\pi)w_c(\pi)A(\beta b,km) \tag{49a}$$

$$+\frac{1}{v_a}\sum_{BP}\sum_{\nu\beta\pi}\sum_{lbrs}A(\nu l,jp)\Phi_{lbr}(0\nu,B\beta,P\pi)X_s(P\pi)A(\beta b,km)\epsilon_{rs}\,. \tag{49b}$$

(49a) can be simplified with the help of (14a) and (22) to

$$-\sum_{rs}\sum_{\alpha\beta\pi}\sum_{abc}[\alpha a,\beta b,\pi c]A(\alpha a,jp)A(\beta b,km)A(\pi c,rs)\eta_{rs}\,. \tag{50}$$

(49b) can be transformed using (14b′) and (28b) to

$$\sum_{\nu}\sum_{lrs}[c(\nu l,[km,rs])+A(\nu l,jp)(\nu s,km)\delta_{lr}+A(\nu l,km)(\nu s,jp)\delta_{lr}]\epsilon_{rs}\,. \tag{51}$$

Collecting the terms, $A_{(jp),(km)}$ from lattice theory is

$$\begin{aligned}A_{(jp),(km)}=&\hat{c}_{[jk,pm]}-\sum_{\nu}\sum_{l}(\nu l,jp)A(\nu l,km)\\&+\sum_{rs}\epsilon_{rs}\{\hat{c}_{jk,[rs],pm}+\sum_{\nu}\sum_{l}\{A(\nu l,rs)(c(\nu l,[jp,km])+c(\nu l,[km,jp]))-[\nu l,[jk,pm]]\}\\&+[A(\nu k,rs)(\nu l,jp)\delta_{lm}+A(\nu j,rs)(\nu l,km)\delta_{lp}]+\{(\nu l,rs)[A(\nu k,jp)\delta_{lm}+A(\nu j,km)\delta_{lp}]\}\\&+A(\nu l,jp)\{(\nu s,km)\delta_{lr}-[\nu l,(km),(rs)]\}+A(\nu l,km)\{(\nu s,jp)\delta_{lr}-[\nu l,(jp),(rs)]\}\\&+A(\nu l,jp)c(\nu l,[km,rs])-\sum_{\nu\beta\gamma}\sum_{abc}[\nu a,\beta b,\gamma c]A(\nu a,jp)A(\beta b,km)A(\gamma c,rs)\}\,.\end{aligned} \tag{52}$$

If the lattice has no inter-lattice displacement the only terms present in (52) are $\hat{c}_{[jk,pm]}$ and $\sum_{rs}\epsilon_{rs}\hat{c}_{jk,[rs],pm}$. Now $A_{(jp),(km)}+A_{(jm),(kp)}$ from lattice theory must be equal to the same quantity on macroscopic elasticity theory. So

$$\begin{aligned}&\hat{c}_{[jk,pm]}+\hat{c}_{[jk,mp]}+\sum_{rs}\epsilon_{rs}[\hat{c}_{jk,[rs],pm}+\hat{c}_{jk,[rs],mp}]\\&\quad=c_{pj,mk}+c_{mj,pk}+\sum_{rs}\epsilon_{rs}[c_{pj,mk,rs}+c_{mj,pk,rs}+2c_{pm,rs}\delta_{jk}+(c_{ps,mk}+c_{ms,pk})\delta_{rj}+(c_{pj,ms}+c_{mj,ps})\delta_{rk}]\,.\end{aligned} \tag{53}$$

Taking the term of zero order in ϵ,

$$c_{pj,mk}+c_{mj,pk}=2\hat{c}_{[jk,pm]}\,. \tag{54}$$

This leads to the Kun-Huang relation, i.e., $\hat{c}_{[jk,pm]}$ is symmetric in $(jk)\leftrightarrow(pm)$. The $c_{pj,mk}$ can be expressed in terms of $\hat{c}_{[jk,pm]}$ and this leads to Eq. (11).

Comparing the coefficients of ϵ_{rs} and using (54) we get

$$2[\hat{c}_{jk,[rs],pm}-\hat{c}_{[sk,pm]}\delta_{rj}-\hat{c}_{[js,pm]}\delta_{rk}]-2c_{pm,rs}\delta_{jk}=c_{pj,mk,rs}+c_{mj,pk,rs}\,. \tag{55}$$

The quantity on the left is symmetric in r and s from the rotational invariance relations for an infinite lattice. The left-hand side must also be symmetric in $(jp)\leftrightarrow(km)$. This is the Kun-Huang relation on the third-order coupling parameters. $c_{jp,km,rs}$ can be expressed in terms of $\hat{c}_{jk,[rs],pm}$ as in (17).

For the nonprimitive lattice in which interlattice displacements are present we can write

$$\bar{c}_{pj,mk}=c_{pj,mk}+d_{pj,mk}\,, \tag{56a}$$

$$\bar{c}_{pj,mk,rs}=c_{pj,mk,rs}+d_{pj,mk,rs}\,. \tag{56b}$$

Here $c_{pj,mk}$ and $c_{pj,mk,rs}$ satisfy (54) and (55). Comparing (56) and (52), we get

$$-\sum_{\nu}\sum_{l}[(\nu l,jp)A(\nu l,km)+(\nu l,jm)A(\nu l,kp)]=d_{pj,mk}+d_{mj,pk}\,. \tag{57}$$

Since $-\sum_{\nu}\sum_{l}(\nu l,jp)A(\nu l,km)$ has the same symmetry as $d_{pj,mk}$

$$d_{pj,mk}=-\sum_{\nu}\sum_{l}(\nu l,jp)A(\nu l,km)\,, \tag{58}$$

$$\begin{aligned}&\sum_{\nu}\sum_{l}\{A(\nu l,rs)\{-2[\nu l,[jk,pm]]+c(\nu l,[jk,pm])+c(\nu l,[km,jp])+c(\nu l,[kp,jm])+c(\nu l,[jm,kp])\}\\&\quad+A(\nu k,rs)[(\nu l,jp)\delta_{lm}+(\nu l,jm)\delta_{lp}]+A(\nu j,rs)[(\nu l,km)\delta_{lp}+(\nu l,kp)\delta_{lm}]\\&\quad+(\nu l,rs)[A(\nu k,jp)\delta_{lm}+A(\nu k,jm)\delta_{lp}+A(\nu j,km)\delta_{lp}+A(\nu j,km)\delta_{lm}]\\&\quad-\sum_{\nu\beta\gamma}\sum_{abc}[\nu a,\beta b,\gamma c]A(\gamma c,rs)[A(\nu a,jp)A(\beta b,km)+A(\nu a,jm)A(\beta b,kp)]\\&\quad+A(\nu l,jp)\{(\nu s,km)\delta_{lr}+(\nu l,ms)\delta_{rk}-[\nu l,(km),(rs)]\}+A(\nu l,jm)\{(\nu s,kp)\delta_{lr}+(\nu l,ps)\delta_{rk}-[\nu l,(kp),(rs)]\}\\&\quad+A(\nu l,kp)\{(\nu s,jm)\delta_{lr}+(\nu l,ms)\delta_{rj}-[\nu l,(jm),(rs)]\}+A(\nu l,km)\{(\nu s,jp)\delta_{lr}+(\nu l,ps)\delta_{rj}-[\nu l,(jp)l(rs)]\}\\&\quad+A(\nu l,jp)c(\nu l,[km,rs])+A(\nu l,jm)c(\nu l,[kp,rs])\}=d_{pj,mk,rs}+d_{mj,pk,rs}+2d_{pm,rs}\delta_{jk}\,.\end{aligned} \tag{59}$$

The right-hand side is symmetric with respect to $(jp) \leftrightarrow (km)$ and $(r \leftrightarrow s)$. The left-hand side is obviously symmetric with respect to $(jp) \leftrightarrow (km)$. If it should be symmetric with respect to $(r \leftrightarrow s)$,

$$[vl,(km),(rs)]-(vs,km)\delta_{lr}-(vl,ms)\delta_{rk}$$

must be symmetric with respect to $(r \leftrightarrow s)$. This follows from the rotational invariance conditions on third-order coupling parameters.

We can solve for $d_{pj,mk,rs}$ from (59) by adding the equation obtained by interchanging p with j and subtracting the equation obtained by interchanging j with m. The expressions for $\bar{c}_{jp,km}$ and $\bar{c}_{jp,km,rs}$ obtained thus from the long-wave method agree with the expressions (26) and (27) from the method of homogeneous deformation.

The theoretical expressions developed in this paper are being applied to analyze the experimental results on the third-order elastic constants of Ge and Si in terms of the third-order coupling parameters.

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Temperature Dependence of Density-of-States Effective Mass and the Electronic and Phonon Contributions to Thermal Resistance of Doped Si-Ge Alloys at High Temperatures

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The electronic polar and dipolar thermal conductivity of both n- and p-type Si-Ge alloys with different carrier concentrations are calculated in the temperature range 300 to 1100°K. With carrier concentration remaining constant, the nature of the scattering mechanism is determined from the temperature dependence of the conductivity mobility. The scattering parameter being known, the temperature dependences of the reduced Fermi level and the density-of-states effective mass are determined from thermoelectric measurements on these samples by Dismukes *et al.* These temperature variations are taken into account in the calculation of the contribution of the electron-phonon interaction to the thermal resistance of the doped Si-Ge alloys. The thermal conductivities due to longitudinal phonons and transverse phonons are calculated separately, and there is good agreement between the calculated temperature dependences of the total phonon conductivity and the experimentally obtained values of thermal conductivity minus the electronic thermal conductivity. The dilatational deformation potential is found to increase with the increase in the carrier concentration and the reduced Fermi potential. The dipolar contribution is found to be significant only at temperatures above 700°K and for n-type alloys, for which the doping is comparatively low.

I. INTRODUCTION

RECENTLY, it has been observed that doping of Si-Ge alloys[1] reduces the lattice thermal conductivity. This has been interpreted in terms of scattering of phonons by free charge carriers. At high temperatures polar and dipolar contributions to thermal resistance due to electrons and holes also become important. The lattice thermal conductivity at such high temperatures is usually obtained by subtracting the electronic contribution from the experimentally observed total thermal conductivity. In highly doped materials phonons are also scattered by ionized impurities, but this contribution towards thermal resistance is negligible. The influence of phonon-electron interaction on lattice thermal conductivity has been shown by Steigmeier and Abeles[2] to be substantial in doped Si-Ge alloys. This contribution is estimated by assuming the additivity of reciprocal relaxation times due to different scattering mechanisms of phonons, such as phonon-phonon scattering (umklapp and normal), scattering of phonons by defects, and phonon-electron scattering. The effective relaxation time thus obtained is used to determine the phonon conductivity in the formalism of Callaway.[3] The expression for the phonon-electron relaxation time for the electrons in the parabolic band involves the knowledge of the reduced Fermi potential, the density-of-states effective mass,

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