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Relationship between Two-Body Interatomic Potentials in a Lattice Model and Elastic Constants[*]

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General equations for the elastic constants associated with a crystal model in which the energy is given by two-body atom-atom interactions and volume-dependent terms are derived for monatomic solids. It is shown that noncentral interactions which require a choice of initial coordinate system do not necessarily give rise to an energy function which is invariant to homogeneous rotations. For central two-body forces, generalized Cauchy relations are defined. Explicit applications of these equations are given for short-ranged central forces in an hcp lattice and noncentral forces in the fcc lattice.

I. INTRODUCTION

A considerable effort has been expended on lattice-defect calculations using two-body interatomic forces and computer-simulation techniques.[1] Elastic-constant data are commonly used as experimental input for developing the interatomic potential for a particular material. The majority of this work has been applied to cubic structures and has used central forces to approximate atom-atom interactions. The equations relating elastic constants and interatomic potentials for these cases are well known and of long standing[2] although some subtleties pertaining to these equations are not well understood. In the present paper, the general relations between elastic constants and two-body forces are developed, and the detailed relations are then given for central forces in hexagonal materials and for noncentral forces in fcc monatomic materials.

II. THEORY

The bond energy per unit undeformed volume in a monatomic crystal is given by a sum over two-body atom-atom interactions:

$$E_b = (1/2\Omega_0)\textstyle\sum_m \phi(\vec{r}^{\,m}) \,, \tag{1}$$

where Ω_0 is the undeformed atomic volume, $\phi(\vec{r}^{\,m})$ is the potential-energy function for two atoms separated by the vector $\vec{r}^{\,m}$, and the sum is taken over the position vector of all lattice atoms relative to an atom at the origin. For small displacements, a Taylor expansion of E_b yields

$$E_b = \frac{1}{2\Omega_0}\sum_m \left\{ \phi(\vec{r}^{\,m})\Big|_0 + \frac{\partial\phi(\vec{r}^{\,m})}{\partial r_j^m}\Big|_0 u_j^m + \frac{1}{2}\,\frac{\partial^2\phi(\vec{r}^{\,m})}{\partial r_j^m\,\partial r_l^m}\Big|_0 u_j^m u_l^m + \cdots \right\} , \tag{2}$$

where r_j^m is a Cartesian component of $\vec{r}^{\,m}$, $\vec{a}^{\,m}$ is the undeformed value of $\vec{r}^{\,m}$, $\vec{u}^{\,m}$ is the displacement vector $\vec{u}^{\,m} = \vec{r}^{\,m} - \vec{a}^{\,m}$, and summation is implied by repeated indices. The evaluation is at the undeformed lattice positions. For a homogeneous deformation, the nine strain parameters $\alpha_{ij} = \partial u_j^m/\partial a_i^m$ are constant, i.e., are independent of m, and $u_i^m = a_j^m \alpha_{ji}$. Thus, for a homogeneous deformation,

$$E_b = A + \alpha_{ij}A_{ij} + \tfrac{1}{2}\alpha_{ij}\alpha_{kl}A_{ijkl} + \cdots \,, \tag{3a}$$

where

$$A = \frac{1}{2\Omega_0}\sum_m \phi(\vec{r}^{\,m})\big|_0 \,, \tag{3b}$$

$$A_{ij} = \frac{1}{2\Omega_0}\sum_m \frac{\partial\phi(\vec{r}^{\,m})}{\partial r_j^m}\Big|_0 a_i^m \,, \tag{3c}$$

$$A_{ijkl} = \frac{1}{2\Omega_0}\sum_m \frac{\partial^2\phi(\vec{r}^{\,m})}{\partial r_j^m\,\partial r_l^m}\Big|_0 a_i^m a_k^m \ . \tag{3d}$$

The equilibrium conditions for a lattice with this energy function are $(\partial E/\partial\alpha_{ij})|_0 = 0$, or, equivalently, that the energy is independent of terms linear in the strain parameters. It is assumed that the α_{ij}'s are zero or of the same order of magnitude. Unless $A_{ij} = 0$, this energy function does not satisfy the equilibrium conditions. Equilibrium can be attained under more general conditions by adding a volume-dependent energy contribution $E_v = P(V/V_0)^n$, where P is a constant, V is the deformed and V_0 the undeformed volume. As a function of the strain parameters, E_v is given by

$$E_v = P(1 + n\alpha_{ii} + \tfrac{1}{2}n^2\alpha_{ii}\alpha_{jj} - \tfrac{1}{2}n\alpha_{ij}\alpha_{ji} + \cdots) \,. \tag{4}$$

The total energy $E = E_b + E_v$ is then

$$E = A + P + \alpha_{ij}(A_{ij} + nP\delta_{ij}) + \tfrac{1}{2}\alpha_{ij}\alpha_{kl}(A_{ijkl} + n^2P\delta_{ij}\delta_{kl} - nP\delta_{il}\delta_{jk}) + \cdots \,, \tag{5}$$

with δ_{ij} the Kronecker δ.

The resultant equilibrium conditions are

$$A_{ij} + nP\delta_{ij} = 0 \ . \tag{6}$$

These conditions impose restrictions on the potential: The diagonal terms of A_{ij} must be equal and the off-diagonal terms must be zero. If the potential-energy function and lattice symmetry are such that these conditions are not fulfilled, a simple volume-dependent energy contribution cannot lead to equilibrium. If these conditions are satisfied, Eq. (6) can be used to determine the value of P required for equilibrium.

The nine independent strain parameters α_{ij} can be written as six symmetric parameters $\epsilon_{ij}=\frac{1}{2}\times(\alpha_{ij}+\alpha_{ji})$ corresponding to pure deformation and three antisymmetric parameters $\gamma_{ij}=\frac{1}{2}(\alpha_{ij}-\alpha_{ji})$ corresponding to pure rotation. Since $\alpha_{ij}=\epsilon_{ij}+\gamma_{ij}$, Eq. (5) is

$$\begin{aligned} E=A+P+(\epsilon_{ij}+\gamma_{ij})(A_{ij}+nP\delta_{ij}) \\ +\tfrac{1}{2}(\epsilon_{ij}+\gamma_{ij})(\epsilon_{kl}+\gamma_{kl}) \\ \times(A_{ijkl}+n^2P\delta_{ij}\delta_{kl}-nP\delta_{il}\delta_{jk})+\cdots\ . \end{aligned} \tag{7}$$

Equilibrium with respect to pure rotation only requires that A_{ij} be symmetric, while equilibrium with respect to pure deformation leads to the conditions given by Eq. (6).

With ΔE given by $E-A-P$, and with the equilibrium conditions satisfied, Eq. (7) becomes

$$\begin{aligned} \Delta E=\tfrac{1}{2}\epsilon_{ij}\epsilon_{kl}(A_{ijkl}+n^2P\delta_{ij}\delta_{kl}-nP\delta_{il}\delta_{jk}) \\ +\tfrac{1}{2}(\epsilon_{ij}\gamma_{kl}+\gamma_{ij}\epsilon_{kl})A_{ijkl} \\ +\tfrac{1}{2}\gamma_{ij}\gamma_{kl}(A_{ijkl}-nP\delta_{il}\delta_{jk})+\cdots\ . \end{aligned} \tag{8}$$

The energy will be independent of pure rotations only if the sum of the last two terms is zero. This requirement (which is discussed below) places a condition on the potential that

$$A_{ijkl}-A_{jikl}=nP(\delta_{il}\delta_{jk}-\delta_{ik}\delta_{jl})\ . \tag{9}$$

The question arises as to whether the condition of invariance of the energy function to pure rotation should be applied. The forces which produce an interatomic potential in a crystal are fixed to the lattice structure. Thus, when the lattice rotates as a whole, physically the interactions rotate with the lattice. The energy function in the present calculation does not allow for this. The lattice is rotated against the noncentral forces fixed at the initial coordinate frame. Therefore, the use of noncentral interactions implies that the noncentral potential must be rotated with the lattice for a homogeneous rotation, and that the noncentral interactions used for a given lattice orientation must only be applied to situations in which the homogeneous deformation does not produce rotation of the lattice as a whole. In the present development, this means that only pure deformation is considered, i.e., $\gamma_{ij}=0$, $\epsilon_{ij}=\alpha_{ij}=\alpha_{ji}$, and Eq. (9) is not applied. Equation (8) is then simplified to

$$\Delta E=\tfrac{1}{2}\epsilon_{ij}\epsilon_{kl}(A_{ijkl}+n^2P\delta_{ij}\delta_{kl}-nP\delta_{il}\delta_{jk})+\cdots\ . \tag{10}$$

For a system initially in equilibrium classical elasticity theory yields[3]

$$\Delta E=\tfrac{1}{2}\epsilon_{ij}\epsilon_{kl}C_{ijkl}+\cdots\ , \tag{11}$$

where C_{ijkl} is the elastic-constant tensor. Recent papers pertaining to the thermodynamics of elasticity theory[4,5] indicate that the Lagrangian strain parameter $\eta_{ij}=\epsilon_{ij}+\frac{1}{2}\alpha_{ik}\alpha_{jk}$ (the symmetric finite-strain parameters introduced by Murnaghan[6]) should be used rather than ϵ_{ij}, but, in the present case, the same results are obtained with either choice of deformation parameter. The elastic-constant tensor is commonly given as

$$C_{ijkl}=\left.\frac{\partial\Delta E}{\partial\epsilon_{ij}\,\partial\epsilon_{kl}}\right|_0\ , \tag{12}$$

and it would appear that this result follows directly from Eq. (11). This relation is misleading, however, and considerable care must be exercised in the use of Eqs. (11) and (12). The difficulty arises from the symmetry of the strain parameters, i.e., there are only six independent strain parameters, not nine, and $\epsilon_{ij}=\epsilon_{ji}$. For example,

$$\left.\frac{\partial^2\Delta E}{\partial\epsilon_{12}^2}\right|_0=(C_{1212}+C_{1221}+C_{2121}+C_{2112})\ .$$

The potential-energy function is related to the elastic-constant tensor by setting Eqs. (10) and (11) equal. With the above discussion in mind, and with $C_{ijkl}=C_{klij}=C_{jikl}$ and $A_{ijkl}=A_{klij}$, this equality leads to

$$\begin{aligned} C_{ijkl}=\tfrac{1}{4}(A_{ijkl}+A_{ijlk}+A_{jikl}+A_{jilk}) \\ +n^2P\delta_{ij}\delta_{kl}-\tfrac{1}{2}nP(\delta_{il}\delta_{jk}+\delta_{ik}\delta_{jl})\ . \end{aligned} \tag{13}$$

If the conditions given by Eq. (9) hold, Eq. (13) reduces to

$$C_{ijkl}=A_{ijkl}+n^2P\delta_{ij}\delta_{kl}-nP\delta_{il}\delta_{jk}\ . \tag{14}$$

This result, which appears to be a direct consequence of equating Eqs. (10) and (11), is valid only in the case in which the energy equation is independent of pure rotations.

These equations can be readily extended to the situation where there are several contributions to the volume dependence, i.e., $E_v=\sum_q P_q(V/V_0)^{n_q}$. The equilibrium conditions are

$$A_{ij}+\delta_{ij}\textstyle\sum_q n_q P_q=0\ , \tag{15}$$

and the elastic constants are given by

$$\begin{aligned} C_{ijkl}=\tfrac{1}{4}(A_{ijkl}+A_{ijlk}+A_{jikl}+A_{jilk}) \\ +\textstyle\sum_q n_q^2 P_q\delta_{ij}\delta_{kl}-\tfrac{1}{2}\sum_q n_q P_q(\delta_{il}\delta_{jk}+\delta_{ik}\delta_{jl})\ . \end{aligned} \tag{16}$$

These equations will be used in the examples in Sec. III.

III. CENTRAL POTENTIAL

In the case of a central potential $\phi = \phi(r)$,

$$\frac{\partial\phi}{\partial r_j} = \frac{r_j}{r}\,\frac{\partial\phi}{\partial r}\,, \tag{17}$$

$$\frac{\partial^2\phi}{\partial r_l\,\partial r_j} = \frac{r_j r_l}{r^2}\left(\frac{\partial^2\phi}{\partial r^2} - \frac{1}{r}\,\frac{\partial\phi}{\partial r}\right) + \delta_{jl}\,\frac{1}{r}\,\frac{\partial\phi}{\partial r}\,. \tag{18}$$

With the notation $\phi'_m \equiv [\partial\phi(r^m)/\partial r^m]|_0$ and $\phi''_m \equiv [\partial^2\phi(r^m)/\partial r^{m2}]|_0$, it follows that

$$A_{ij} = \frac{1}{2\Omega_0}\sum_m \frac{1}{a^m}\,\phi'_m a_i^m a_j^m\,, \tag{19}$$

$$A_{ijkl} = \frac{1}{2\Omega_0}\sum_m\left[\frac{1}{(a^m)^2}\left(\phi''_m - \frac{1}{a^m}\,\phi'_m\right)a_i^m a_j^m a_k^m a_l^m + \delta_{jl}\,\frac{1}{a^m}\,\phi'_m a_i^m a_k^m\right]. \tag{20}$$

Then, with the definition

$$B_{ijkl} \equiv \frac{1}{2\Omega_0}\sum_m \frac{1}{(a^m)^2}\left(\phi''_m - \frac{1}{a^m}\,\phi'_m\right)a_i^m a_j^m a_k^m a_l^m\,, \tag{21}$$

we have

$$A_{ijkl} = B_{ijkl} + \delta_{jl} A_{ik}\,. \tag{22}$$

The matrix B_{ijkl} is symmetric with respect to all changes of indices, and with the equilibrium condition $A_{ik} = -\sum_q n_q P_q \delta_{ik}$, the elastic constants are

$$C_{ijkl} = B_{ijkl} + \textstyle\sum_q n_q^2 P_q \delta_{ij}\delta_{kl} - \sum_q n_q P_q(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})\,. \tag{23}$$

As a generalization of the Cauchy conditions,

$$C_{ijkl} - C_{ikjl} = \textstyle\sum_q n_q(n_q+1)P_q(\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl})\,, \tag{24}$$

or in Voigt notation,

$$C_{23} - C_{44} = C_{31} - C_{55} = C_{12} - C_{66} = \textstyle\sum_q n_q(n_q+1)P_q\,, \tag{25}$$

$$C_{14} - C_{56} = C_{25} - C_{64} = C_{36} - C_{45} = 0\,.$$

Thomas[7] has pointed out that, with a model similar to that used here, the commonly accepted relation[8] $C_{12} - C_{44} = 2P$ does not necessarily hold for short-ranged forces in fcc and bcc materials. The requirement for this relation to hold for a material with central forces is that there be only one volume-dependent term with $n = 1$. These equations can be applied directly to obtain the relations between elastic constants and a central potential in any lattice structure.

A. fcc

For the well-known case of a central potential between nearest neighbors in an fcc lattice,[2]

$$A_{11} = A_{22} = A_{33} = \frac{b^2}{\Omega_0}\,\frac{1}{a}\,\phi'\,, \tag{26a}$$

$$A_{12} = A_{23} = A_{31} = 0\,, \tag{26b}$$

where b is the lattice constant (a is the nearest-neighbor distance) and the equilibrium condition is

$$\sum_q n_q P_q = -\frac{b^2}{\Omega_0}\,\frac{1}{a}\,\phi'\,. \tag{27}$$

The subscript denoting evaluation at the initial state is dropped. The equations for the bulk modulus $B = \frac{1}{3}(C_{11} + 2C_{12})$ and the shears $C = C_{44}$ and $C' = \frac{1}{2}(C_{11} - C_{12})$ are

$$B = (b^2/3\Omega_0)[\phi'' + (1/a)\phi'] + \textstyle\sum_q n_q^2 P_q\,, \tag{28a}$$

$$C = (b^2/4\Omega_0)[\phi'' + (3/a)\phi']\,, \tag{28b}$$

$$C' = (b^2/8\Omega_0)[\phi'' + (7/a)\phi']\,. \tag{28c}$$

The two shears are independent of the volume contribution, and the common form for B is obtained for a single volume term with $n = 1$. The two shears are sufficient to determine the two potential parameters ϕ'' and $(1/a)\phi'$:

$$(1/a)\phi' = (\Omega_0/b^2)(2C' - C)\,, \tag{29a}$$

$$\phi'' = (\Omega_0/b^2)(7C - 6C')\,, \tag{29b}$$

and the volume-dependent terms are given by

$$\sum n_q P_q = C - 2C'\,, \tag{30a}$$

$$\sum n_q^2 P_q = B - 2C + \tfrac{4}{3}C'\,. \tag{30b}$$

If there is just one volume term,

$$P = (1/n)(C - 2C') \tag{31}$$

and there is a compatibility equation for the elastic constants,

$$n(C - 2C') = B - 2C + \tfrac{4}{3}C'\,. \tag{32}$$

If there are two volume terms,

$$P_1 = \frac{B - 2C + \frac{4}{3}C'}{n_1(n_1 - n_2)} - \frac{n_2(C - 2C')}{n_1(n_1 - n_2)}\,, \tag{33a}$$

$$P_2 = \frac{B - 2C + \frac{4}{3}C'}{n_2(n_2 - n_1)} - \frac{n_1(C - 2C')}{n_2(n_2 - n_1)}\,. \tag{33b}$$

B. hcp

Let r_1 be the nearest-neighbor distance between atoms in different basal planes, r_2 the nearest-neighbor distance between atoms in a basal plane, and $(\partial\phi/\partial r)|_{r_i} = \phi'_i$. If these are the only interactions considered,

$$A_{11} = A_{22} = \frac{a^2}{2\Omega_0}\left(\frac{1}{r_1}\,\phi'_1 + \frac{3}{r_2}\,\phi'_2\right), \tag{34a}$$

$$A_{33} = \frac{3c^2}{4\Omega_0}\,\frac{1}{r_1}\,\phi'_1\,, \tag{34b}$$

$$A_{12}=A_{23}=A_{31}=0\ . \tag{34c}$$

For equilibrium,

$$\frac{1}{r_2}\,\phi_2'=\left(\frac{c^2}{2a^2}-\frac{1}{3}\right)\frac{1}{r_1}\,\phi_1'\ . \tag{35}$$

This condition is satisfied directly for an ideal c/a ratio, but applies a constraint on the potential for nonideal ratios. The elastic constants are

$$C_{11}=\frac{a^4}{8\Omega_0}\left[\frac{1}{r_1^2}\left(\phi_1''-\frac{1}{r_1}\,\phi_1'\right)+\frac{9}{r_2^2}\left(\phi_2''-\frac{1}{r_2}\,\phi_2'\right)\right]+\sum_q n_q^2P_q-2\sum_q n_qP_q\ , \tag{36a}$$

$$C_{12}=\frac{a^4}{24\Omega_0}\left[\frac{1}{r_1^2}\left(\phi_1''-\frac{1}{r_1}\,\phi_1'\right)+\frac{9}{r_2^2}\left(\phi_2''-\frac{1}{r_2}\,\phi_2'\right)\right]+\sum_q n_q^2P_q\ , \tag{36b}$$

$$C_{66}=\tfrac{1}{2}\,(C_{11}-C_{12})\ , \tag{36c}$$

$$C_{33}=\frac{3\,c^4}{16\Omega_0}\,\frac{1}{r_1^2}\left(\phi_1''-\frac{1}{r_1}\,\phi_1'\right)+\sum_q n_q^2P_q-2\sum_q n_qP_q\ , \tag{36d}$$

$$C_{31}=\frac{a^2c^2}{8\Omega_0}\,\frac{1}{r_1^2}\left(\phi_1''-\frac{1}{r_1}\,\phi_1'\right)+\sum_q n_q^2P_q\ , \tag{36e}$$

$$C_{44}=\frac{a^2c^2}{8\Omega_0}\,\frac{1}{r_1^2}\left(\phi_1''-\frac{1}{r_1}\,\phi_1'\right)-\sum_q n_qP_q\ , \tag{36f}$$

and the Cauchy condition in this case gives

$$C_{31}-C_{44}=C_{12}-C_{66}\quad\text{or}\quad C_{31}-C_{44}=\tfrac{3}{2}\,C_{12}-\tfrac{1}{2}\,C_{11}\ . \tag{37}$$

In an analogous manner to the fcc case, the shear parameters $C_a=C_{66}=\frac{1}{2}\,(C_{11}-C_{12})$, $C_b=C_{44}$, and $C_b'=\frac{1}{2}(C_{33}-C_{31})$ are defined, and are given by

$$C_a=\frac{a^4}{24\Omega_0}\left[\frac{1}{r_1^2}\left(\phi_1''+\frac{3(c^2+a^2)}{a^2}\,\frac{1}{r_1}\,\phi_1'\right)+\frac{9}{r_2^2}\,(\phi_2''+\tfrac{3}{2}\phi_2')\right]\ , \tag{38a}$$

$$C_b=\frac{a^2c^2}{8\Omega_0}\left[\frac{1}{r_1^2}\left(\phi_1''+\frac{3c^2+2a^2}{2a^2}\,\frac{1}{r_1}\,\phi_1'\right)\right], \tag{38b}$$

$$C_b'=\frac{(3c^2-2a^2)\,c^2}{32\Omega_0}\left[\frac{1}{r_1^2}\left(\phi_1''+\frac{3c^2+10a^2}{3c^2-2a^2}\,\frac{1}{r_1}\,\phi_1'\right)\right]\ . \tag{38c}$$

With the equilibrium conditions and these relations, the potential parameters are determined, and, again as in the fcc case, are independent of the volume terms:

$$\frac{1}{r_1}\,\phi_1'=\frac{4\Omega_0}{9c^2(c^2-2a^2)}\,[(3c^2-2a^2)C_b-4a^2\,C_b']\ , \tag{39a}$$

$$\frac{1}{r_2}\,\phi_2'=\frac{2\Omega_0(3c^2-2a^2)}{27a^2c^2(c^2-2a^2)}\,[(3c^2-2a^2)\,C_b-4a^2\,C_b']\ , \tag{39b}$$

$$\phi_1''=\frac{4\Omega_0}{9c^2(c^2-2a^2)}\,[2(3c^2+2a^2)\,C_b'-(3c^2+10a^2)\,C_b]\ , \tag{39c}$$

$$\phi_2''=\frac{2\Omega_0}{27a^2c^2(c^2-2a^2)}\,[36c^2(c^2-2a^2)\,C_a+4a^2(9c^2-2a^2)\,C_b'-(9c^2-10a^2)\,(3c^2+2a^2)\,C_b]\ . \tag{39d}$$

The volume-dependent terms are related by

$$\sum n_qP_q=\frac{1}{3(c^2-2a^2)}\,[4a^2C_b'-(3c^2-2a^2)\,C_b]\ , \tag{40a}$$

$$\sum n_q^2P_q+\sum n_qP_q=B_a-\tfrac{5}{3}\,C_a=B_b-\tfrac{2}{3}\,C_b'-C_b\ , \tag{40b}$$

where the bulk moduli are defined by $B_a=\frac{1}{3}\,(C_{11}+2C_{12})$ and $B_b=\frac{1}{3}\,(C_{33}+C_{31})$. If there is just one volume term,

$$P=\frac{1}{3n(c^2-2a^2)}\,[4a^2C_b'-(3c^2-2a^2)C_b] \tag{41}$$

and there is a compatibility equation for the elastic constants in addition to that arising from the Cauchy condition:

$$\frac{n}{3(c^2-2a^2)}\,[4a^2\,C_b'-(3c^2-2a^2)\,C_b]=B_a-\tfrac{5}{3}\,C_a+3C_b-2C_b'=B_b+2C_b-\tfrac{8}{3}\,C_b'\ . \tag{42}$$

The equality on the right-hand side of the two expressions in Eqs. (40b) and (42) expresses the relation imposed by the Cauchy condition.

For an ideal c/a ratio, these relations simplify to

$$C_a=\frac{a^2}{12\Omega_0}\left(5\phi_1''+\frac{19}{r_1}\,\phi_1'\right)\ , \tag{43a}$$

$$C_b=\frac{a^2}{3\Omega_0}\left(\phi_1''+\frac{5}{r_1}\,\phi_1'\right), \tag{43b}$$

$$C_b'=\frac{a^2}{2\Omega_0}\left(\phi_1''+\frac{3}{r_1}\,\phi_1'\right)\ , \tag{43c}$$

$$\frac{1}{r_1}\,\phi_1'=\frac{\Omega_0}{2a^2}\,(3C_b-2C_b')\ , \tag{44a}$$

$$\phi_1''=\frac{\Omega_0}{2a^2}\,(10C_b'-9C_b)\ , \tag{44b}$$

$$\sum_q n_qP_q=2C_b'-3C_b\ , \tag{45a}$$

$$\sum_q n_q^2P_q=B_a-\tfrac{5}{3}\,C_a+3C_b-2C_b'=B_q+2C_b-\tfrac{8}{3}\,C_b'\ . \tag{45b}$$

In the case of just one volume term and an ideal c/a ratio,

$$P=(1/n)(2C_b'-3C_b) \tag{46}$$

and the compatibility equation is

$$\begin{aligned} n(2C_b'-3C_b) &= B_a-\tfrac{5}{3}C_a+3C_b-2C_b' \\ &= B_b+2C_b-\tfrac{8}{3}C_b' . \end{aligned} \tag{47}$$

IV. NONCENTRAL POTENTIAL

Very little has been reported in the literature pertaining to the use of noncentral interactions in the construction of potentials for defect calculations. A noncentral potential of the form

$$\phi(\vec{r})=p(r)+q(r)\,w(\theta,\,\phi) \tag{48}$$

has been used in several point-defect calculations for cubic materials[9,10] where $w(\theta,\phi)$ is the cubic harmonic,[11]

$$w(\theta,\,\phi)=\left(\frac{x^4+y^4+z^4}{r^4}-\frac{3}{5}\right)\equiv s-\tfrac{3}{5} . \tag{49}$$

This potential is discussed in the present section.

In the following paragraphs, summation is not implied by repeated indices. Differentiation of the noncentral potential yields

$$\frac{\partial\phi}{\partial r_j}=\frac{r_j}{r}\left(\frac{\partial p}{\partial r}+w\,\frac{\partial q}{\partial r}\right)+q\,\frac{\partial s}{\partial r_j} , \tag{50a}$$

$$\frac{\partial^2\phi}{\partial r_j\,\partial r_l}=\frac{r_jr_l}{r^2}\left[\left(\frac{\partial^2 p}{\partial r^2}+w\,\frac{\partial^2 q}{\partial r^2}\right)-\frac{1}{r}\left(\frac{\partial p}{\partial r}+w\,\frac{\partial q}{\partial r}\right)\right]+\delta_{jl}\,\frac{1}{r}\left(\frac{\partial p}{\partial r}+w\,\frac{\partial q}{\partial r}\right)+\left(r_j\,\frac{\partial s}{\partial r_l}+r_l\,\frac{\partial s}{\partial r_j}\right)\frac{1}{r}\,\frac{\partial q}{\partial r}+\frac{\partial^2 s}{\partial r_j\,\partial r_l}\,q . \tag{50b}$$

With

$$\frac{\partial s}{\partial r_j}=\frac{4r_j^3}{r^4}-\frac{4r_j s}{r^2} , \tag{51a}$$

$$\frac{\partial^2 s}{\partial r_j\,\partial r_l}=\frac{12r_j^2}{r^4}\,\delta_{jl}-\frac{4s}{r^2}\,\delta_{jl}-\frac{16r_jr_l(r_j^2+r_l^2)}{r^6}+\frac{24r_jr_ls}{r^4} \tag{51b}$$

and with the same notation for evaluated derivatives with respect to r as in the discussion of the central potential,

$$A_{ij}=\frac{1}{2\Omega_0}\sum_m\left\{\frac{1}{a^m}\,(p_m'+w_mq_m')+\frac{4q_m}{(a^m)^2}\left[\left(\frac{a_j^m}{a^m}\right)^2-s_m\right]\right\}a_i^m\,a_j^m , \tag{52}$$

$$\begin{aligned} A_{ijkl}=\sum_m\Bigg(&\frac{1}{(a^m)^2}\left((p_m''+w_mq_m'')-\frac{1}{a^m}\,(p_m'+w_mq_m')-8s_m\,\frac{q_m'}{a^m}+24s_m\,\frac{q_m}{(a^m)^2}\right)a_i^m\,a_j^m\,a_k^m\,a_l^m \\ &+\left\{\frac{1}{a^m}\,(p_m'+w_mq_m')+\frac{4q_m}{(a^m)^2}\left[\frac{1}{2}\left(\frac{a_k^m}{a^m}\right)^2+\frac{1}{2}\left(\frac{a_i^m}{a^m}\right)^2-s_m\right]\right\}\delta_{jl}\,a_i^m\,a_k^m \\ &+4\left(\frac{q_m'}{a^m}-\frac{4q_m}{(a^m)^2}\right)\left(\frac{(a_j^m)^2+(a_l^m)^2}{(a^m)^4}\right)a_i^m\,a_j^m\,a_k^m\,a_l^m+\frac{4q_m}{(a^m)^4}\,[3(a_j^m)^2-\tfrac{1}{2}\,(a_k^m)^2-\tfrac{1}{2}(a_i^m)^2]\,\delta_{jl}\Bigg) . \end{aligned} \tag{53}$$

The second term in the summation for A_{ijkl} is $\frac{1}{2}\delta_{jl}(A_{ik}+A_{ki})$, so that, with the equilibrium conditions and with $f(r)=p(r)+w(\theta,\,\phi)|_0\,q(r)$,

$$\begin{aligned} A_{ijkl}=\frac{1}{2\Omega_0}\sum_m\frac{1}{(a^m)^2}\Bigg\{&\left[f_m''-\frac{1}{a^m}\,f_m'-8s_m\,\frac{q_m'}{a^m}+24s_m\,\frac{q_m}{(a^m)^2}+4\left(\frac{(a_j^m)^2+(a_l^m)^2}{(a^m)^2}\right)\left(\frac{q_m'}{a^m}-\frac{4q_m}{(a^m)^2}\right)\right]a_i^m\,a_j^m\,a_k^m\,a_l^m \\ &+\frac{4q_m}{(a^m)^2}\,\delta_{jl}\,[3(a_j^m)^2-\tfrac{1}{2}\,(a_i^m)^2-\tfrac{1}{2}(a_k^m)^2]\,a_i^m\,a_k^m\Bigg\}-\sum_q n_qP_q\,\delta_{ik}\,\delta_{jl} . \end{aligned} \tag{54}$$

The general form for the elastic constants is then

$$C_{ijkl}=\frac{1}{2\Omega_0}\sum_m\frac{1}{(a^m)^2}\left\{\left(f_m''-\frac{1}{a^m}\,f_m'\right)a_i^m\,a_j^m\,a_k^m\,a_l^m+\frac{2q_m'}{a^m}\left(\frac{(a_i^m)^2+(a_j^m)^2+(a_k^m)^2+(a_l^m)^2}{(a^m)^2}-4s_m\right)a_i^m\,a_j^m\,a_k^m\,a_l^m\right.$$

$$+\frac{q_m}{(a^m)^2}\left[3(\delta_{ik}+\delta_{il}+\delta_{jk}+\delta_{jl})+24s_m-8\left(\frac{(a_i^m)^2+(a_j^m)^2+(a_k^m)^2+(a_l^m)^2}{(a^m)^2}\right)\right]a_i^m a_j^m a_k^m a_l^m$$

$$-\frac{q_m}{2(a^m)^2}\{\delta_{ik}a_j^m a_l^m[(a_j^m)^2+(a_l^m)^2]+\delta_{il}a_j^m a_k^m[(a_j^m)^2+(a_l^m)^2]+\delta_{jk}a_i^m a_l^m[(a_i^m)^2+(a_l^m)^2]$$

$$+\delta_{jl}a_i^m a_k^m[(a_i^m)^2+(a_k^m)^2]\}\Big\}+\sum_q n_q^2 P_q\delta_{ij}\delta_{kl}-\sum_q n_q P_q(\delta_{il}\delta_{jk}+\delta_{ik}\delta_{jl})\ . \qquad (55)$$

For the case of a noncentral potential between nearest neighbors in a fcc lattice

$$A_{11}=A_{22}=A_{33}=\frac{b^2}{\Omega_0}\frac{1}{a}f'\ , \qquad (56a)$$

$$A_{12}=A_{23}=A_{31}=0\ , \qquad (56b)$$

where b is the lattice constant (a is the nearest-neighbor distance), and the equilibrium condition is

$$\sum_q n_q P_q=-\frac{b^2}{\Omega_0}\frac{1}{a}f'\ . \qquad (57)$$

The subscript denoting evaluation at the initial state is dropped. The equations for the bulk modulus $B=\frac{1}{3}(C_{11}+2C_{12})$ and the two shears $C=C_{44}$ and $C'=\frac{1}{2}(C_{11}-C_{12})$ are

$$B=\frac{b^2}{3\Omega_0}\left(f''-\frac{1}{a}f'\right)+\sum_q n_q^2 P_q\ , \qquad (58a)$$

$$C=\frac{b^2}{4\Omega_0}\left(f''+\frac{3}{a}f'\right)-\frac{q}{\Omega_0}\ , \qquad (58b)$$

$$C'=\frac{b^2}{8\Omega_0}\left(f''+\frac{7}{a}f'\right)+\frac{3q}{\Omega_0}\ . \qquad (58c)$$

These equations are very similar to those from the central-potential case [Eq. (28)]. The dependence on the radial factor f is the same here as for the central potential ϕ, the shears are independent of the volume contribution, and the dependence of the bulk modulus on the volume contribution is the same. The noncentral terms do not enter into the equation for the bulk modulus, but do affect the shears, as would be expected.

V. DISCUSSION

Equations have been derived which can be applied to a monatomic crystal of any symmetry to obtain the relations between elastic constants and potential-energy functions for a model which contains two-body interactions and arbitrary volume dependence. The primary results are given by Eqs. (15) and (16), which express an equilibrium condition which imposes a constraint on the potential, and the explicit relationship between the elastic constants, the potential-energy function (which may be central or noncentral), and the volume-dependent terms. Examples for central and noncentral potentials in a fcc lattice and central potentials in a hcp lattice are given.

Wallace[5] has recently presented a detailed discussion of the thermoelasticity of stressed materials including a review of various expansions which have been used for the energy density in a stressed elastic media. The present treatment, which is similar to that given by Huang,[12] is not as general as the theory developed by Wallace, but the defining equations are consistent with those given by Wallace at zero initial stress and proposed earlier by Brugger.[4] The basic difference in the present treatment is that rotational-invariance conditions are not applied to the energy function arising from bond interactions. It should be emphasized that, for potentials which do give rise to rotational invariance of the energy function, the same results are obtained here as if the rotational-invariance condition were applied. The only difference exists for noncentral interactions which require a choice of initial coordinate system.

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Cyclotron Resonance in Tellurium

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A study of the temperature dependence of the position, shape, and width of the submillimeter cyclotron-resonance absorption line has provided data which have been compared with the predictions of several theoretical models. The data favor the valence-band structure of tellurium as proposed by Weiler. This shows that the Landau levels are not parallel in the k_z direction. It also shows that the transitions between Landau levels at low temperature occur at the valence-band maximum on the camel back and not at $k_z = 0$. Previous experiments, two other theoretical models, and previous attempts to fit band parameters are reviewed and evaluated.

I. INTRODUCTION

The structure of the upper valence band of tellurium has a camel-back shape for its $E(k_z)$ dependence as first proposed by Betbeder-Matibet and Hulin[1] and rigorously derived by Doi, Nakao, and Kamimura[2-4] using the $\vec{k}\cdot\vec{p}$ method. Attempts to determine the valence-band parameters of the camel-back model have generated a number of different theoretical approaches which differ in their higher-order terms and also in the values of their constants. It was not possible to decide from the available experimental data which of the models is the most realistic.

Therefore, the principal objective of the present experiments was to carry out a careful study of submillimeter cyclotron resonance as a function of temperature and to compare the results with the temperature dependence predicted by each of the models. We measured position, width, and shape of the cyclotron-resonance line at temperatures from a few degrees to 120 K. Consistent results could only be obtained by eliminating extraneous influences which had been present in previous experiments[5-12] owing to specimens of insufficient purity. So we selected very pure, Czochralski-grown specimens in which impurity absorption and changes in the transmission, caused by a variation of the refractive index with the magnetic field, are practically absent and therefore do not interfere with the study of the cyclotron absorption line. Our spectrum therefore consisted of a single absorption line when the magnetic field was parallel to the trigonal axis of the crystal. Thus we were able to obtain precise data and to compare these data with the theoretical predictions. The additional details of the experimental conditions and results are described in Secs. II and III.

The comparison of our low-temperature experimental results with three theoretical approaches described in Secs. IV and V does not favor model W2[9] nearly as well as model W1.[13] We conclude that for the magnetic field parallel to the c axis of the crystal the energy separation of the Landau levels is not constant, but a function of the wave vector parallel to the magnetic field; i.e., the Landau levels are not equidistant as a function of k_z. Both model W1 and model J[10] predict nonequidistant Landau levels but the quantitative comparison favors model W1, which seems to be the most realistic one so far. However, further improvements in the theoretical approach are desirable.

From our detailed calculations we can also assert that the transitions between Landau levels at low temperatures occur at the valence-band maxi-