PHYSICAL REVIEW B

SOLID STATE

THIRD SERIES, VOL. 7, NO. 4 15 FEBRUARY 1973

Thermal Expansion at a Crystal Surface*

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(Received 27 April 1972)

A lattice-dynamical theory is presented of the thermal expansion of a Bravais crystal slab. The theory incorporates the static temperature-independent relaxation of the interplanar spacings in the vicinity of the crystal surface, the homogeneous temperature-dependent deformation (thermal expansion) of the crystal arising from cubic anharmonic terms in the crystal potential energy, and temperature-dependent changes in the interplanar spacings at the surface arising from the same source. Numerical estimates of these effects are presented for a nearest- and next-nearest-neighbor central-force model of α-iron.

I. INTRODUCTION

In recent years there has been considerable interest in the experimental and theoretical study of structural and dynamical properties of crystal surfaces. The work up to a few years ago has been summarized in a recent review article.[1] Nevertheless, until now, no general analysis has appeared of the thermal expansion at a crystal surface. To our knowledge, only Allen *et al.*[2] have studied this effect, but only by essentially numerical methods. In this paper we present a lattice-dynamical theory of the thermal expansion of a Bravais crystal slab. Our analysis has the advantage of being analytical and straightforward. We are primarily concerned with the displacements of the mean positions of atoms near the surface from the mean position that these atoms would have in the bulk of the crystal. If these displacements are determined by minimizing the static energy, we shall call them the static displacements. If they are determined by minimizing the total free energy, including vibrational contributions, we shall call them the dynamic displacements.

The free surfaces of our slab are created by setting to zero all interactions which cross each of two planes passing through an infinite lattice parallel to a (001) plane but not containing any particles. The particles in the surface layer and in the adjacent interior layers are then acted upon by unbalanced forces, and consequently suffer displacements to new equilibrium positions.

The static temperature-independent displacements of surface atoms have been computed by several authors.[2-9] Our theory incorporates the static relaxation of the interplanar spacings in the vicinity of the crystal surface, the homogeneous temperature-dependent deformation (thermal expansion) of the crystal arising from the cubic anharmonic terms in the crystal potential energy, and temperature-dependent changes in the interplanar spacings at the surface arising from the same source. Numerical estimates of these effects are presented for a nearest- and next-nearest-neighbor central-force model of a slab of α-iron bounded by (001) faces.

Our analysis also gives for the first time the temperature dependence of the dynamical displacements.

In Sec. II, we obtain the static and dynamical contributions to the potential energy of a crystal slab. In Sec. III, the dynamic contribution to the free energy is also derived analytically. In Sec. IV, we give the general analytic expressions for the thermal expansion of a crystal slab. In Sec. V, we apply them to a (001)-free-surface slab of α-iron, with nearest- and next-nearest-neighbor central-force interactions between atoms.

II. STATIC AND DYNAMICAL CONTRIBUTION TO POTENTIAL ENERGY

We begin by expanding the potential energy of a Bravais crystal slab in powers of the displacements of the atoms from the equilibrium positions they would have had if they formed part of an infinitely extended, or cyclic, crystal instead of a slab:

$$\Phi=\Phi_0+\sum_{\substack{l\\ \alpha}}\Phi_\alpha(l)\,\xi_\alpha(l)+\tfrac12\sum_{\substack{ll'\\ \alpha\beta}}\Phi_{\alpha\beta}(ll')\,\xi_\alpha(l)\,\xi_\beta(l')+\tfrac16\sum_{\substack{ll'l''\\ \alpha\beta\gamma}}\Phi_{\alpha\beta\gamma}(ll'l'')\,\xi_\alpha(l)\,\xi_\beta(l')\,\xi_\gamma(l'')+\cdots . \qquad (2.1)$$

In this expression Φ_0 is the value of the static potential energy. $\xi_\alpha(l)$ is the α Cartesian component of the displacement of the lth atom. The first-order atomic force constants $\{\Phi_\alpha(l)\}$ are nonzero only for sites l near the surfaces, because a first-rank tensor invariant under the operations of the point group of the lattice site to which it refers must vanish identically for an infinitely extended Bravais crystal, which includes the inversion among the symmetry operations at each site. $\Phi_{\alpha\beta}(ll')$ and $\Phi_{\alpha\beta\gamma}(ll'l'')$ are the harmonic and anharmonic force constants, respectively.

We suppose that $\xi_\alpha(l)$ is the resultant of three terms, the first of which describes a homogeneous deformation of the crystal, the second of which represents the dynamical displacements of the atoms due to the free surfaces, and the third of which describes arbitrary displacements of the atoms from their new positions in the deformed crystal:

$$\xi_\alpha(l)=s_\alpha(l)+d_\alpha(l)+u_\alpha(l)\ , \qquad (2.2)$$

where

$$s_\alpha(l)=\sum_\lambda \epsilon_{\alpha\lambda}\,x_\lambda(l)\ . \qquad (2.3)$$

The vector $\vec{x}(l)$ is the vector to the equilibrium position of the lth atom in the undeformed crystal. The parameters $\{\epsilon_{\alpha\lambda}\}$ describe a homogeneous deformation of the crystal, and are not assumed here to be symmetric in α and λ. We now substitute Eq. (2.2) into Eq. (2.1) and collect terms in powers of the displacement components $\{u_\alpha(l)\}$, to obtain

$$\Phi=\Phi_s+\Phi_D\ , \qquad (2.4)$$

where

$$\begin{aligned}\Phi_s=\Phi_0&+\sum_{l\alpha}\Phi_\alpha(l)\,[s_\alpha(l)+d_\alpha(l)]\\&+\tfrac12\sum_{\substack{ll'\\ \alpha\beta}}\Phi_{\alpha\beta}(ll')\,[s_\alpha(l)+d_\alpha(l)]\,[s_\beta(l')+d_\beta(l')]\\&+\tfrac16\sum_{\substack{ll'l''\\ \alpha\beta\gamma}}\Phi_{\alpha\beta\gamma}(ll'l'')\,[s_\alpha(l)+d_\alpha(l)]\,[s_\beta(l')+d_\beta(l')]\\&\qquad\times[s_\gamma(l'')+d_\gamma(l'')]+\cdots \qquad (2.5)\end{aligned}$$

and

$$\Phi_D=\sum_{l\alpha}\hat{\Phi}_\alpha(l)\,u_\alpha(l)+\tfrac12\sum_{\substack{ll'\\ \alpha\beta}}\hat{\Phi}_{\alpha\beta}(ll')\,u_\alpha(l)\,u_\beta(l')+\tfrac16\sum_{\substack{ll'l''\\ \alpha\beta\gamma}}\hat{\Phi}_{\alpha\beta\gamma}(ll'l'')\,u_\alpha(l)\,u_\beta(l')\,u_\gamma(l'')+\cdots , \qquad (2.6)$$

with

$$\begin{aligned}\hat{\Phi}_\alpha(l)=\Phi_\alpha(l)&+\sum_{l'\beta}\Phi_{\alpha\beta}(ll')\,[s_\beta(l')+d_\beta(l')]\\&+\tfrac12\sum_{\substack{l'l''\\ \beta\gamma}}\Phi_{\alpha\beta\gamma}(ll'l'')\,[s_\beta(l')+d_\beta(l')]\\&\qquad\times[s_\gamma(l'')+d_\gamma(l'')]+\cdots , \qquad (2.7)\end{aligned}$$

$$\hat{\Phi}_{\alpha\beta}(ll')=\Phi_{\alpha\beta}(ll')+\sum_{l''\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')\times[s_\gamma(l'')+d_\gamma(l'')]+\cdots , \qquad (2.8)$$

$$\hat{\Phi}_{\alpha\beta\gamma}(ll'l'')=\Phi_{\alpha\beta\gamma}(ll'l'')+\cdots . \qquad (2.9)$$

To first order in the deformation parameters $\{\epsilon_{\alpha\lambda}\}$ and the displacements $\{d_\alpha(l)\}$, the vibrational contribution to the Helmholtz free energy obtained from the dynamical part of the crystal potential energy, Eq. (2.6), can be written in the form

$$F(T)=F^{(0)}(T)+\tfrac12\sum_{\substack{ll'l''\\ \alpha\beta\gamma}}\Phi_{\alpha\beta\gamma}(ll'l'')\,\langle u_\alpha(l)\,u_\beta(l')\rangle\times[s_\gamma(l'')+d_\gamma(l'')]+\cdots . \qquad (2.10)$$

Explicit expressions for $F^{(0)}(T)$ and the correlation function $\langle u_\alpha(l)\,u_\beta(l')\rangle$ will be obtained in Sec. III. There, the mean positions of the atoms at temperature T are defined by the condition

$$\langle u_\alpha(l)\rangle=0\ . \qquad (2.11)$$

This gives the following relation between the $\{\epsilon_{\alpha\lambda}\}$ and the $\{d_\alpha(l)\}$:

$$\begin{aligned}\Phi_\alpha(l)&+\sum_{l'\beta}\Phi_{\alpha\beta}(ll')\,[s_\beta(l')+d_\beta(l')]+F_\alpha(l\,|\,T)\\&+\tfrac12\sum_{l'\beta}\sum_{l''\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')\,[s_\beta(l')+d_\beta(l')]\\&\qquad\times[s_\gamma(l'')+d_\gamma(l'')]+\cdots=0\ . \qquad (2.12)\end{aligned}$$

The expression for $F_\alpha(l\,|\,T)$ will be given in Sec. III. In Sec. IV, this equation will be solved for $\{d_\alpha(l)\}$ as a function of the $\{\epsilon_{\alpha\lambda}\}$ and the result will be substituted into the expression for the total free energy of the crystal:

$$\mathfrak{F}(T)=\Phi_s+F(T)\ . \qquad (2.13)$$

The deformation parameters $\{\epsilon_{\alpha\lambda}\}$ will then be obtained in Sec. IV by minimizing this free energy.

III. DYNAMIC CONTRIBUTION TO FREE ENERGY

If we add the kinetic energy of the atoms to the dynamic contribution to the potential energy of a deformed crystal slab, given by Eq. (2.6), we can write the vibrational Hamiltonian for the slab as

$$H = H_0 + H_A \,, \tag{3.1a}$$

where

$$H_0 = \sum_{l\alpha} \frac{p_\alpha^2(l)}{2M} + \frac{1}{2} \sum_{l\alpha} \sum_{l'\beta} \hat{\Phi}_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') \,, \tag{3.1b}$$

$$H_A = \sum_{l\alpha} \hat{\Phi}_\alpha(l) u_\alpha(l) + \tfrac{1}{6} \sum_{l\alpha} \sum_{l'\beta} \sum_{l''\gamma} \hat{\Phi}_{\alpha\beta\gamma}(ll'l'') u_\alpha(l) \times u_\beta(l') u_\gamma(l'') + \cdots \tag{3.1c}$$

through cubic anharmonic terms. Here $p_\alpha(l)$ is the α Cartesian component of the momentum of atom l, and M is its mass.

It is now convenient to introduce the eigenvalues and eigenvectors of the matrix $\hat{D}_{\alpha\beta}(ll') = \hat{\Phi}_{\alpha\beta}(ll')/M$ by

$$\sum_{l'\beta} \hat{D}_{\alpha\beta}(ll') C_\beta^{(s)}(l') = \Omega_s^2 C_\alpha^{(s)}(l) \,, \quad s = 1, 2, \ldots, 3N_a \tag{3.2}$$

where the $\{C_\alpha^{(s)}(l)\}$ can be chosen to be real and to satisfy

$$\sum_{l\alpha} C_\alpha^{(s)}(l) C_\alpha^{(s')}(l) = \delta_{ss'} \,, \tag{3.3a}$$

$$\sum_{s} C_\alpha^{(s)}(l) C_\beta^{(s)}(l') = \delta_{ll'} \delta_{\alpha\beta} \,, \tag{3.3b}$$

and N_a is the total number of atoms in the slab.

These eigenvectors and eigenvalues can be used to generate a normal coordinate transformation

$$u_\alpha(l) = \left(\frac{\hbar}{2M}\right)^{1/2} \sum_s \frac{C_\alpha^{(s)}(l)}{(\Omega_s)^{1/2}} A_s \,, \tag{3.4a}$$

$$p_\alpha(l) = \frac{1}{i}\left(\frac{\hbar M}{2}\right)^{1/2} \sum_s (\Omega_s)^{1/2} C_\alpha^{(s)}(l) B_s \,, \tag{3.4b}$$

where $A_s = A_s^\dagger$ and $B_s = -B_s^\dagger$ are the phonon field and momentum operators, respectively.

In terms of these operators the Hamiltonian H_0 and H_A take the forms

$$H_0 = \sum_s \tfrac{1}{4}\hbar\Omega_s [B_s^\dagger B_s + A_s^\dagger A_s] \,, \tag{3.5a}$$

$$H_A = \sum_s V_s A_s + \sum_{s_1 s_2 s_3} V_{s_1 s_2 s_3} A_{s_1} A_{s_2} A_{s_3} \,, \tag{3.5b}$$

where

$$V_s = \left(\frac{\hbar}{2M\Omega_s}\right)^{1/2} \sum_{l\alpha} \hat{\Phi}_\alpha(l) C_\alpha^{(s)}(l) \,, \tag{3.6a}$$

$$V_{s_1 s_2 s_3} = \frac{1}{6}\left(\frac{\hbar}{2M}\right)^{3/2} \frac{1}{(\Omega_{s_1}\Omega_{s_2}\Omega_{s_3})^{1/2}} \sum_{\substack{ll'l'' \\ \alpha\beta\gamma}} \hat{\Phi}_{\alpha\beta\gamma}(ll'l'') \times C_\alpha^{(s_1)}(l) C_\beta^{(s_2)}(l') C_\gamma^{(s_3)}(l'') \,. \tag{3.6b}$$

We will treat the Hamiltonian H_A as a perturbation on the Hamiltonian H_0.

The contribution to the vibrational free energy from the harmonic Hamiltonian H_0 is

$$F_0(T) = k_B T \sum_s \ln[2\sinh(\hbar\Omega_s/2k_B T)] \,. \tag{3.7}$$

The contribution to the vibrational free energy from the anharmonic Hamiltonian H_A is given by[10]

$$F(T) - F_0(T) = \frac{1}{\beta} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \int_0^\beta d\beta_1 \cdots \int_0^\beta d\beta_n \times \langle T\tilde{V}(\beta_1)\cdots\tilde{V}(\beta_n)\rangle_{oc} \,, \tag{3.8}$$

where $\beta = (k_B T)^{-1}$,

$$\tilde{V}(\beta) = e^{\beta H} H_A e^{-\beta H} \,, \tag{3.9}$$

T is an operator which orders operators from right to left in order of increasing arguments, and the angular brackets $\langle\cdots\rangle_{oc}$ denote an average over the canonical ensemble defined by the Hamiltonian H_0, and if the terms in the perturbation series (3.8) are represented diagrammatically, only the contribution from connected, topologically distinct diagrams is retained. By topologically distinct we mean diagrams which do not differ from each other only by a permutation of the "times" $\beta_1, \cdots, \beta_n$ at which the interactions described by $\tilde{V}(\beta)$ occur.

If only the contributions of zero and first order in $V_{s_1 s_2 s_3}$ are included in the anharmonic contribution to the vibrational free energy, it is the conbutions associated with the diagrams in Fig. 1 which must be calculated. The contribution associated with the diagram in Fig. 1(a) is

$$\delta F_1(T) = -\tfrac{1}{2}\beta \sum_s V_s D_s(0) V_s \,, \tag{3.10}$$

where

$$D_s(i\omega_l) = \frac{2\Omega_s}{\beta\hbar} \frac{1}{\Omega_s^2 - (i\omega_l)^2} \,, \qquad \omega_l = \frac{2\pi l}{\beta\hbar} \,. \tag{3.11}$$

The contribution associated with the diagram in Fig. 1(b) is

$$\delta F_2(T) = -3\beta \sum_{ss_1} \sum_{l=-\infty}^{\infty} V_s D_s(0) V_{ss_1 s_1} D_{s_1}(i\omega_l) \,. \tag{3.12}$$

Combining Eqs. (3.7), (3.10), and (3.12), we obtain for the vibrational contribution to the free energy

$$F(T) = k_B T \sum_s \ln[2\sinh(\hbar\Omega_s/2k_B T)] - \tfrac{1}{2}\beta \sum_s V_s D_s(0) V_s - 3\beta \sum_{ss_1} \sum_{l=-\infty}^{\infty} V_s D_s(0) V_{ss_1 s_1} D_{s_1}(i\omega_l) \,, \tag{3.13}$$

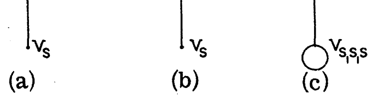

FIG. 1. Diagrams giving the first contributions to the vibrational free energy from the anharmonic Hamiltonian H_A [Eq. (3.1c)].

through terms linear in the cubic anharmonic force constants.

The mean positions of the atoms at temperature T are defined by the condition

$$\langle u_\alpha(l)\rangle = 0 \,, \tag{3.14}$$

where the average is evaluated with respect to the canonical ensemble defined by the Hamiltonian (3.1b). In view of Eq. (3.4a), and the orthogonality of the eigenvectors $\{C_\alpha^{(s)}(l)\}$, it follows that the condition (3.14) is equivalent to the condition

$$\langle A_s\rangle = 0 \,. \tag{3.15}$$

The perturbation expansion for the expectation value of any operator O can be written in the form

$$\langle O\rangle = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^{\beta} d\beta_1 \cdots \int_0^{\beta} d\beta_n \,\langle T\tilde{V}(\beta_1)\cdots \times \tilde{V}(\beta_n)\,\tilde{O}(0)\rangle_{oc} \,. \tag{3.16}$$

In the present case we find that

$$\langle A_s\rangle = -\beta\left(D_s(0)\,V_s + 3D_s(0)\sum_{s_1}\sum_{l=-\infty}^{\infty} V_{ss_1s_1} D_{s_1}(i\omega_l)\right) . \tag{3.17}$$

Combining Eqs. (3.15) and (3.17), we obtain the equation determining the mean positions of the atoms in the deformed crystal at temperature T:

$$V_s + 3\sum_{s_1}\sum_{l=-\infty}^{\infty} V_{ss_1s_1} D_{s_1}(i\omega_l) = 0 \,. \tag{3.18}$$

By the use of Eqs. (3.15) and (3.17), we can simplify the free-energy expression (3.13). From these equations we obtain the result that in the equilibrium configuration,

$$\sum_s V_s\langle A_s\rangle = 0 = -\beta\sum_s V_s D_s(0)\,V_s - 3\beta\sum_{ss_1}\sum_{l=-\infty}^{\infty} V_s D_s(0)\,V_{ss_1s_1} D_{s_1}(i\omega_l) \,. \tag{3.19}$$

Consequently, we can rewrite Eq. (3.13) as

$$F(T) = k_BT\sum_s \ln[2\sinh(\hbar\Omega_s/2k_BT)] - \tfrac{3}{2}\beta\sum_{ss_1}\sum_{l=-\infty}^{\infty} V_s D_s(0)\,V_{ss_1s_1} D_{s_1}(i\omega_l) \,. \tag{3.20}$$

If, finally, we use Eq. (3.18) in (3.20), we obtain

$$F(T) = k_BT\sum_s \ln[2\sinh(\hbar\Omega_s/2k_BT)] + \tfrac{9}{2}\beta\sum_{ss_1s_2}\sum_{l_1,l_2=-\infty}^{\infty} D_{s_1}(i\omega_{l_1})\,V_{s_1s_1s}\,D_s(0) \times V_{ss_2s_2} D_{s_2}(i\omega_{l_2}) \,. \tag{3.21}$$

The second term on the right-hand side of this equation is of second order in the cubic anharmonic force constants. Therefore, if we require the vibrational contribution to the free energy only to first order in the cubic anharmonic force constants, it is given by

$$F(T) = k_BT\sum_s \ln[2\sinh(\hbar\Omega_s/2k_BT)] \,. \tag{3.22}$$

[In fact, the contribution to $F(T)$ given by the second term on the right-hand side of Eq. (3.21) is cancelled by the contribution associated with the diagram in Fig. 1(c), which we have not considered explicitly here. More generally, it can be shown that when the condition (3.15) is taken into account, there is no contribution to the vibrational part of the free energy from any diagram which can be divided into two pieces by cutting a single free-phonon line.[10]]

We now recall that the $\{\hat{\Phi}_{\alpha\beta}(ll')\}$ are the atomic force constants for the deformed crystal. In terms of the eigenvectors and eigenvalues of the dynamical matrix of the undeformed slab, $D_{\alpha\beta}(ll') = \Phi_{\alpha\beta}(ll')/M$,

$$\sum_{l'\beta} D_{\alpha\beta}(ll')\,B_\beta^{(s)}(l') = \omega_s^2 B_\alpha^{(s)}(l), \quad s = 1, 2, \ldots, 3N_a \tag{3.23}$$

where

$$\sum_{l\alpha} B_\alpha^{(s)}(l)\,B_\alpha^{(s')}(l) = \delta_{ss'} \,, \tag{3.24a}$$

$$\sum_s B_\alpha^{(s)}(l)\,B_\beta^{(s)}(l') = \delta_{ll'}\,\delta_{\alpha\beta} \,, \tag{3.24b}$$

we find, using first-order perturbation theory, that

$$\Omega_s^2 = \omega_s^2 + \frac{1}{M}\sum_{l\alpha}\sum_{l'\beta}\sum_{l''\gamma} B_\alpha^{(s)}(l)\,\Phi_{\alpha\beta\gamma}(ll'l'') \times B_\beta^{(s)}(l')\,[s_\gamma(l'') + d_\gamma(l'')] \,, \tag{3.25a}$$

$$C_\alpha^{(s)}(l) = B_\alpha^{(s)}(l) + \frac{1}{M}\sum_{s'(\neq s)}\sum_{l'\beta}\sum_{l''\gamma}\sum_{l'''\delta} B_\alpha^{(s')}(l) \times \frac{B_\beta^{(s')}(l')\,\Phi_{\beta\gamma\delta}(l'l''l''')\,B_\delta^{(s)}(l'')}{\omega_s^2 - \omega_{s'}^2}\,[s_\delta(l''') + d_\delta(l''')] \,. \tag{3.25b}$$

With these results we can rewrite $F(T)$ as

$$F(T) = k_BT\sum_s \ln[2\sinh(\hbar\omega_s/2k_BT)] + \frac{1}{M}\sum_s \frac{\hbar}{4\omega_s}\sum_{l\alpha}\sum_{l'\beta}\sum_{l''\gamma} B_\alpha^{(s)}(l)\,\Phi_{\alpha\beta\gamma}(ll'l'')\,B_\beta^{(s)}(l')\coth(\hbar\omega_s/2k_BT)\,[s_\gamma(l'') + d_\gamma(l'')] \,, \tag{3.26}$$

to first order in the cubic anharmonic force constants.

If we make use of Eqs. (3.6), the subsidiary condition (3.18), which relates $d_\alpha(l)$ and $\epsilon_{\alpha\lambda}$, takes the form

$$\hat{\Phi}_\alpha(l) + \frac{\hbar}{2M}\sum_s\sum_{l'\beta}\sum_{l''\gamma} \hat{\Phi}_{\alpha\beta\gamma}(ll'l'')\,\frac{C_\beta^{(s)}(l')\,C_\gamma^{(s)}(l'')}{2\Omega_s}\coth\left(\frac{\hbar\Omega_s}{2k_BT}\right) = 0 \,. \tag{3.27}$$

Recalling that $\hat{\Phi}_{\alpha\beta\gamma}(ll'l'')$ is already of first order in the cubic anharmonic force constants, we can replace $C_\alpha^{(s)}(l)$ and Ω_s by $B_\alpha^{(s)}(l)$ and ω_s in this equation, respectively. Then, with the definition (2.7), we obtain finally the condition

$$\Phi_\alpha(l)+\sum_{l'\beta}\Phi_{\alpha\beta}(ll')[s_\beta(l')+d_\beta(l')]+\tfrac{1}{2}\sum_{l'\beta}\sum_{l''\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')[s_\beta(l')+d_\beta(l')][s_\gamma(l'')+d_\gamma(l'')]$$
$$+\frac{\hbar}{2M}\sum_s\sum_{l'\beta}\sum_{l''\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')B_\beta^{(s)}(l')B_\gamma^{(s)}(l'')\frac{\coth(\hbar\omega_s/2k_BT)}{2\omega_s}=0\ . \quad (3.28)$$

By using the result that[1]

$$\langle u_\alpha(l)u_\beta(l')\rangle=\frac{\hbar}{2M}\sum_s\frac{B_\alpha^{(s)}(l)B_\beta^{(s)}(l')}{\omega_s}\coth(\tfrac{1}{2}\beta\hbar\omega_s) \quad (3.29)$$

and by calling

$$F^{(0)}(T)=k_BT\sum_s\ln[2\sinh(\hbar\omega_s/2k_BT)]\ , \quad (3.30)$$

we can rewrite $F(T)$ as

$$F(T)=F^{(0)}(T)+\tfrac{1}{2}\sum_{\substack{ll'l''\\ \alpha\beta\gamma}}\Phi_{\alpha\beta\gamma}(ll'l'')\langle u_\alpha(l)u_\beta(l')\rangle\times[s_\gamma(l'')+d_\gamma(l'')]\ . \quad (3.31)$$

Let us define

$$F_\gamma(l''\mid T)=\tfrac{1}{2}\sum_{\substack{ll'\\ \alpha\beta}}\langle u_\alpha(l)u_\beta(l')\rangle\Phi_{\alpha\beta\gamma}(ll'l'')\ . \quad (3.32)$$

With this notation, the condition (3.28) which relates $d_\alpha(l)$ and $\epsilon_{\alpha\lambda}$ can also be written as

$$\Phi_\alpha(l)+\sum_{l'\beta}\Phi_{\alpha\beta}(ll')[s_\beta(l')+d_\beta(l')]+F_\alpha(l\mid T)+\tfrac{1}{2}\sum_{l'\beta}\sum_{l''\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')[s_\beta(l')+d_\beta(l')]\times[s_\gamma(l'')+d_\gamma(l'')]=0\ . \quad (3.33)$$

In Sec. IV, we will solve this last equation by iteration to obtain $d_\alpha(l)$, which will be substituted into the expression for the total free energy $F(T)$ [Eq. (2.13)], which will then be minimized with respect to the $\{\epsilon_{\alpha\lambda}\}$, yielding the temperature dependence of the deformation parameters, and in turn of the $\{d_\alpha(l)\}$.

IV. THERMAL EXPANSION OF A CRYSTAL SLAB

To obtain the thermal expansion, we need to calculate the $\{d_\alpha(l)\}$ and the $\{\epsilon_{\alpha\lambda}\}$. Equation (3.33) will give $d_\alpha(l)$ as a function of $\epsilon_{\alpha\lambda}$. We will insert this value of $d_\alpha(l)$ in the total free energy

$$\mathfrak{F}(T)=\Phi_s+F(T)\ ,$$

and minimize the latter with respect to the $\{\epsilon_{\alpha\lambda}\}$, obtaining in this way these deformation parameters, and in turn the $\{d_\alpha(l)\}$. From Eqs. (2.5) and (3.31), the total free energy is

$$\mathfrak{F}(T)=\tilde{\Phi}_0(T)=\sum_{l\alpha}\Phi_\alpha(l)[s_\alpha(l)+d_\alpha(l)]+\tfrac{1}{2}\sum_{\substack{ll'\\ \alpha\beta}}\Phi_{\alpha\beta}(ll')[s_\alpha(l)+d_\alpha(l)][s_\beta(l')+d_\beta(l')]$$
$$+\tfrac{1}{6}\sum_{\substack{ll'l''\\ \alpha\beta\gamma}}\Phi_{\alpha\beta\gamma}(ll'l'')[s_\alpha(l)+d_\alpha(l)][s_\beta(l')+d_\beta(l')][s_\gamma(l'')+d_\gamma(l'')]$$
$$+\tfrac{1}{2}\sum_{\substack{ll'l''\\ \alpha\beta\gamma}}\Phi_{\alpha\beta\gamma}(ll'l'')\langle u_\alpha(l)u_\beta(l')\rangle[s_\gamma(l'')+d_\gamma(l'')]+\dots\ , \quad (4.1)$$

where

$$\tilde{\Phi}_0(T)=\Phi_0+F^{(0)}(T)\ .$$

Let us rewrite Eq. (3.33) in the form

$$\sum_{l'\beta}\Phi_{\alpha\beta}(ll')d_\beta(l')=P_\alpha(l)-\tfrac{1}{2}\sum_{l'\beta}\sum_{l''\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')\times[s_\beta(l')+d_\beta(l')][s_\gamma(l'')+d_\gamma(l'')]\ , \quad (4.2)$$

where we have defined

$$P_\alpha(l)=\sum_{\beta\mu}G_{\alpha\beta\mu}(l)\epsilon_{\beta\mu}-F_\alpha(l\mid T)-\Phi_\alpha(l)\ , \quad (4.3)$$

$$G_{\alpha\beta\mu}(l)=-\sum_{l'}\Phi_{\alpha\beta}(ll')x_\mu(l')$$
$$=\sum_{l'}\Phi_{\alpha\beta}(ll')x_\mu(ll')\ , \quad (4.4)$$

with

$$x_\mu(ll')=x_\mu(l)-x_\mu(l')\ . \quad (4.5)$$

Equation (4.2) can be solved by iteration, solving it first without the quadratic term in the $\{s_\beta(l')+d_\beta(l')\}$ as shown in Refs. 11 and 12, then substituting this solution in the right-hand side of Eq. (4.2) and solving again as before. We only keep in the solution linear terms in the anharmonic force constants, remembering that the $\{\epsilon_{\alpha\lambda}\}$ are linear in the $\{\Phi_{\alpha\beta\gamma}(ll'l'')\}$. One iteration is enough to see that the quadratic term in the $\{s_\beta(l')+d_\beta(l')\}$ only contributes one term linear in the $\{\Phi_{\alpha\beta\gamma}(ll'l'')\}$, but quadratic in the $\{\Phi_\alpha(l)\}$. This quadratic term in the $\{s_\beta(l')+d_\beta(l')\}$ gives a temperature-independent anharmonic correction to the static relaxation obtained with $P_\alpha(l)=-\Phi_\alpha(l)$. For this reason, we are neglecting this quadratic term, keeping only the leading terms $\{\Phi_\alpha(l)\}$ for the static relaxation. In a more quantitative study, this correction should be kept, as being linear in the anharmonic force constants and possibly of the same order of magnitude at $T=0\,^\circ\mathrm{K}$ as $F_\alpha(l\,|\,T)$, for l being near the free surfaces. But here our main aim is to discuss the physics of each of these effects rather than performing very accurate numerical estimations.

A. Dynamic Displacements $d_\alpha(l)$

To solve Eq. (4.2), one can take advantage of the symmetries of the slab studied. In the case of a slab with (001) free surfaces, the translational symmetry of each site implies that the $\{P_\alpha(l)\}$ [Eq. (4.3)] and $\{d_\alpha(l)\}$ are independent of l_1 and l_2 and functions only of l_3 and that

$$\Phi_{\alpha\beta}(l_1, l_2, l_3; l_1', l_2', l_3') = \Phi_{\alpha\beta}(l_1-l_1', l_2-l_2', l_3; 0, 0, l_3') \ . \qquad (4.6)$$

The point symmetries of each site and group-theory considerations[1] enable us to find that the only nonzero elements of the $\{G_{\alpha\beta\mu}(l_3)\}$ [Eq. (4.4)] and $\{\epsilon_{\beta\mu}\}$ are the following ones:

$$\begin{aligned} &G_{xxz}(l_3)=G_{yyz}(l_3)\ , \quad G_{xzx}(l_3)=G_{yzy}(l_3)\ ,\\ &G_{zxx}(l_3)=G_{zyy}(l_3)\ , \quad G_{zzz}(l_3)\ , \end{aligned} \qquad (4.7)$$

$$\epsilon_{xx}=\epsilon_{yy}\ , \qquad \epsilon_{zz}\ . \qquad (4.8)$$

In the same way one finds that

$$F_\alpha(l_3\,|\,T)=\delta_{\alpha z}F_z(l_3\,|\,T)\ , \qquad (4.9)$$

$$\Phi_\alpha(l_3)=\delta_{\alpha z}\Phi_z(l_3)\ , \qquad (4.10)$$

$$P_\alpha(l_3)=\delta_{\alpha z}P_z(l_3)\ , \qquad (4.11\mathrm{a})$$

$$P_z(l_3)=\sum_\beta G_{z\beta\beta}(l_3)\,\epsilon_{\beta\beta}-F_z(l_3\,|\,T)-\Phi_z(l_3)\ , \qquad (4.11\mathrm{b})$$

$$d_\alpha(l_3)=\delta_{\alpha z}d_z(l_3)\ . \qquad (4.12)$$

Using these results and defining

$$\overline{\Phi}_{\alpha\beta}(l_3, l_3')=\sum_{l_1'l_2'}\Phi_{\alpha\beta}(l_1-l_1', l_2-l_2', l_3; 0, 0, l_3')\ , \qquad (4.13)$$

we can rewrite Eq. (4.2) in the following form:

$$\sum_{l_3'}\overline{\Phi}_{zz}(l_3, l_3')\,d_z(l_3')=P_z(l_3)\ . \qquad (4.14)$$

In this equation the quadratic term in the $\{s_\beta(l')+d_\beta(l')\}$ appearing in Eq. (4.2) is neglected, for the reasons discussed following Eq. (4.5). In terms of $\underline{\mathrm{U}}$, the inverse of $\underline{\overline{\Phi}}_{zz}$,

$$\underline{\mathrm{U}}\ \underline{\overline{\Phi}}_{zz}=\underline{\mathrm{I}}\ , \qquad (4.15)$$

the solution of Eq. (4.14) is

$$d_z(l_3)=\sum_{l_3}U(l_3, l_3')\,P_z(l_3')\ . \qquad (4.16)$$

From (4.16) and (4.11b) we see that $d_z(l_3)$ will be a linear function of ϵ_{xx}, ϵ_{yy}, and ϵ_{zz}. We will see below that the solution (4.16) has the form

$$d_z(l_3)=[A_z\epsilon_{zz}+A_x(\epsilon_{xx}+\epsilon_{yy})+B]\,x_z(l_3)+C_z(l_3)\ . \qquad (4.17)$$

In (4.17), $C_z(l_3)$ represents contributions to $d_z(l_3)$ localized near the free surfaces. The coefficients A_z, A_x, B are independent of l_3 and are different for different crystals. The form (4.17) will enable us to obtain a general expression for the $\{\epsilon_{\alpha\lambda}\}$.

B. $\epsilon_{\alpha\lambda}$ for a Slab

Let us now substitute $d_\alpha(l)$, solution (4.17), into the total free energy $\mathfrak{F}(T)$ [Eq. (4.1)] and minimize $\mathfrak{F}(T)$ with respect to $\epsilon_{\nu\lambda}$. In this way we obtain

$$\begin{aligned}\frac{\partial\mathfrak{F}(T)}{\partial\epsilon_{\nu\lambda}}=0=\sum_{l\alpha}\frac{\partial[s_\alpha(l)+d_\alpha(l)]}{\partial\epsilon_{\nu\lambda}}\Big(&\Phi_\alpha(l)+\sum_{l'\beta}\Phi_{\alpha\beta}(ll')\\ &\times[s_\beta(l')+d_\beta(l')]+\tfrac{1}{2}\sum_{ll'l''}\sum_{\beta\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')\langle u_\beta(l')u_\gamma(l'')\rangle\\ &+\tfrac{1}{2}\sum_{ll'l''}\sum_{\beta\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')[s_\beta(l')+d_\beta(l')][s_\gamma(l'')+d_\gamma(l'')]\Big)\ .\end{aligned} \qquad (4.18)$$

By remarking that $\epsilon_{\nu\lambda}$ and $d_\alpha(l)$ in the bulk will be of first order in the anharmonic force constants, and that $\Phi_\alpha(l)$ has nonzero elements only in the vicinity of the free surfaces, (4.18) may be rewritten after neglecting higher-order terms in $\Phi_{\alpha\beta\gamma}(ll'l'')$ and terms proportional to the ratio of surface area to volume, of $O(N_s/N_a)$, where N_s is the number of surface atoms, as

$$\begin{aligned}\frac{\partial\mathfrak{F}(T)}{\partial\epsilon_{\nu\lambda}}=\sum_{l\alpha}\frac{\partial[s_\alpha(l)+d_\alpha(l)]}{\partial\epsilon_{\nu\lambda}}\Big(&\sum_{l'\beta}\Phi_{\alpha\beta}(ll')[s_\beta(l')+d_\beta(l')]\\ &+\tfrac{1}{2}\sum_{ll'l''}\sum_{\beta\gamma}\Phi_{\alpha\beta\gamma}(ll'l'')\langle u_\beta(l')u_\gamma(l'')\rangle\Big)=0\ ,\end{aligned} \qquad (4.18')$$

where

$$\begin{aligned}\frac{\partial[s_\alpha(l)+d_\alpha(l)]}{\partial\epsilon_{\nu\lambda}}=\delta_{\alpha\nu}\,x_\lambda(l)+\delta_{\alpha z}\delta_{\nu\lambda}[&A_z\delta_{\lambda z}\\ &+A_x(\delta_{\lambda x}+\delta_{\lambda y})]\,x_z(l)+\delta_{\alpha z}\frac{\partial C_z(l_3)}{\partial\epsilon_{\nu\lambda}}\ .\end{aligned} \qquad (4.19)$$

Let us insert (4.19) in (4.18′) and use the fact that $G_{\alpha\beta\mu}(l_3)$ [Eq. (4.4)] and $C_z(l_3)$ are nonzero only in the vicinity of the free surfaces and will give terms of the order N_s/N_a, which we neglect. We define also

$$C_{\nu\lambda\beta\mu}=\frac{1}{V}\sum_{ll'}\Phi_{\nu\beta}(ll')\,x_\lambda(l)\,x_\mu(l')\ , \qquad (4.20)$$

which are the ordinary bulk elastic constants,[12] V being the volume of the crystal and

$$F_{\nu\lambda}(T)=\tfrac{1}{2}\sum_{ll'l''}\langle u_\alpha(l)u_\beta(l')\rangle\,\Phi_{\alpha\beta\nu}(ll'l'')\,x_\lambda(l'')\ . \qquad (4.21)$$

Finally (4.18′) takes the form

$$\frac{\partial \mathfrak{F}(T)}{\partial \epsilon_{\nu\lambda}} = V \sum_{\beta\mu} C_{\nu\lambda\beta\mu}\, \epsilon_{\beta\mu} + V \sum_{\beta\mu} C_{zz\beta\mu}\, \epsilon_{\beta\mu}\, \delta_{\nu\lambda} \times [A_z \delta_{\lambda z} + A_x(\delta_{\lambda x} + \delta_{\lambda y})] + V\{C_{\nu\lambda zz} + C_{zzzz}\, \delta_{\nu\lambda} [A_z \delta_{\lambda z} + A_x(\delta_{\lambda x} + \delta_{\lambda y})]\} [A_z \epsilon_{zz} + A_x(\epsilon_{xx} + \epsilon_{yy}) + B] + F_{\nu\lambda}(T) + F_{zz}(T)\, \delta_{\nu\lambda} [A_z + A_x(\delta_{\lambda x} + \delta_{\lambda y})] = 0 \; . \tag{4.18$''$}$$

To solve (4.18″), let us use the fact that by symmetry the only nonzero $\{\epsilon_{\beta\mu}\}$ are $\epsilon_{zz} \neq \epsilon_{xx} = \epsilon_{yy}$ and that in the bulk

$$F_{\nu\lambda}(T) = \delta_{\nu\lambda} F_B(T) + O(N_s/N_a) \; . \tag{4.22}$$

We obtain, in this way,

$$\frac{\partial \mathfrak{F}(T)}{\partial \epsilon_{zz}} = (1 + A_z)\left(V \sum_{\beta} C_{zz\beta\beta}\, \epsilon_{\beta\beta} + F_B(T)\right) + V C_{zzzz} [A_z \epsilon_{zz} + A_x(\epsilon_{xx} + \epsilon_{yy}) + B] = 0 \; , \tag{4.23a}$$

$$\frac{\partial \mathfrak{F}(T)}{\partial \epsilon_{xx}} = V \sum_{\beta} C_{xx\beta\beta}\, \epsilon_{\beta\beta} + F_B(T) + A_x\left(V \sum_{\beta} C_{zz\beta\beta}\, \epsilon_{\beta\beta} + F_B(T)\right) + V(C_{xxzz} + A_x C_{zzzz}) \times [A_z \epsilon_{zz} + A_x(\epsilon_{xx} + \epsilon_{yy}) + B] \; . \tag{4.23b}$$

For cubic crystals, we have

$$C_{\sigma\sigma\sigma\sigma} = C_{11} \; ,$$

$$C_{\sigma\sigma\sigma'\sigma'} = C_{12} \qquad \text{for } \sigma \neq \sigma' \; , \tag{4.24}$$

where C_{11} and C_{12} are the usual elastic constants. Equations (4.23) and (4.24) give two equations for two unknowns ϵ_{zz}, $\epsilon_{xx} = \epsilon_{yy}$:

$$(1 + A_z) C_{11}\, \epsilon_{zz} + 2(C_{12} + C_{11} A_x)\, \epsilon_{xx} = -F_B(T)/V - C_{11} B \; , \tag{4.25a}$$

$$(1 + A_z)(C_{12} + C_{11} A_x)\, \epsilon_{zz} + [C_{11}(1 + 2A_x^2) + C_{12}(1 + 4A_x)]\epsilon_{xx} = -(1 + A_x) F_B(T)/V - B(C_{12} + A_x C_{11}) \; . \tag{4.25b}$$

The solutions of these equations are

$$\epsilon_{xx} = \epsilon_{yy} = -\frac{1}{3V}\, \frac{F_B(T)}{\tilde{B}} + O\left(\frac{N_s}{N_a}\right) , \tag{4.26a}$$

$$\epsilon_{zz} = \frac{1 - 2A_x}{1 + A_z}\, \epsilon_{xx} - \frac{B}{1 + A_z} + O\left(\frac{N_s}{N_a}\right) , \tag{4.26b}$$

where

$$\tilde{B} = \tfrac{1}{3}(C_{11} + 2C_{12}) \tag{4.27}$$

is the bulk modulus in the harmonic approximation. Let us remember that $d_z(l_3)$ [Eq. (4.17)] has a constant thermal expansion term. By adding this term to the ϵ_{zz} given by Eq. (4.26b), we obtain the effective ϵ_{zz} for a slab, which we will call $\hat{\epsilon}_{zz}$:

$$\hat{\epsilon}_{zz} = \epsilon_{zz} + A_z \epsilon_{zz} + 2A_x \epsilon_{xx} + B + O(N_s/N_a) \tag{4.28}$$

or

$$\hat{\epsilon}_{zz} = \epsilon_{xx} + O(N_s/N_a) \; . \tag{4.29}$$

Let us remark that $\epsilon_{xx} = \epsilon_{yy} = \hat{\epsilon}_{zz}$ assume their bulk values when terms of the order of N_s/N_a are negligible. The result (4.26a) is identical to the bulk one obtained by one of us.[13]

In Sec. IV C, we will apply these general results to a slab of a bcc crystal. The $d_z(l_3)$ [Eq. (4.16)] will be obtained by a Green's-function method for a slab extending from $l_3 = 0$ to $l_3 = N$ and created by removing in an infinitely extended crystal all interactions crossing the median planes situated, respectively, between $l_3 = 0$ and -1, and $l_3 = N$ and $N + 1$. This Green's-function method consists of obtaining first the inverse $\underline{G}$ of $\underline{\Phi}_{zz}$ [Eq. (4.15)] for an infinite crystal, and then calculating the inverse $\underline{U}$ of $\underline{\Phi}_{zz}$ for a slab by the usual Dyson relation. We will see that $d_z(l_3)$ may indeed be written in the form (4.17). We will then be able to obtain $\epsilon_{xx} = \epsilon_{yy} = \hat{\epsilon}_{zz}$ from Eq. (4.26a). And by putting back the $\{\epsilon_{\sigma\sigma}\}$ into the expression obtained for $d_z(l_3)$, we will have the temperature-dependent changes in the interplanar spacings.

C. Explicit Expressions for Displacements of Atoms

The results given in Secs. IV A and B are general and can be applied to a slab of any cubic Bravais crystal bounded by (001) free surfaces. They can also be easily transposed for a slab bounded by other than (001) free surfaces.

A central-force approximation will now be used and applied to a bcc crystal. Explicit expressions for the thermal expansion at (001) surface of a slab will be derived in this case.

1. Central-Force Approximation

In a central-force approximation we have

$$\Phi_\alpha(l) = \sum_{l'(\neq l)} \varphi_\alpha(ll') \; , \tag{4.30}$$

with

$$\varphi_\alpha(ll') = x_\alpha(ll')\, D\varphi(r(ll')) \tag{4.31}$$

and

$$D\varphi(r) = (1/r)\, \varphi'(r) \; . \tag{4.32}$$

In this approximation, the harmonic force constants are

$$\Phi_{\alpha\beta}(ll') = -\varphi_{\alpha\beta}(ll') \; , \quad l \neq l'$$

$$\Phi_{\alpha\beta}(ll) = \sum_{l' \neq l} \varphi_{\alpha\beta}(ll') \; , \tag{4.33}$$

with

$$\varphi_{\alpha\beta}(ll') = x_\alpha(ll')\, x_\beta(ll')\, D^2\varphi(r(ll')) + \delta_{\alpha\beta}\, D\varphi(r(ll')) \; , \tag{4.34}$$

where

$$D^2\varphi(r) = (1/r^2)\, \varphi''(r) - (1/r^3)\, \varphi'(r) \; . \tag{4.35}$$

The nonzero anharmonic force constants are

$$\Phi_{\alpha\beta\gamma}(l'l'l)=\Phi_{\alpha\beta\gamma}(l'll')=\Phi_{\alpha\beta\gamma}(ll'l')=-\Phi_{\alpha\beta\gamma}(lll')$$

$$=-\Phi_{\alpha\beta\gamma}(ll'l)=\Phi_{\alpha\beta\gamma}(l'll)=\varphi_{\alpha\beta\gamma}(ll')$$

$$\text{for } l\neq l' , \quad (4.36)$$

$$\Phi_{\alpha\beta\gamma}(lll)=\sum_{l'(\neq l)}\varphi_{\alpha\beta\gamma}(ll') , \quad (4.37)$$

with

$$\varphi_{\alpha\beta\gamma}(ll')=x_\alpha(ll')\,x_\beta(ll')\,x_\gamma(ll')\,D^3\varphi(r(ll'))$$

$$+[x_\alpha(ll')\,\delta_{\beta\gamma}+x_\beta(ll')\,\delta_{\gamma\alpha}+x_\gamma(ll')\,\delta_{\alpha\beta}]\,D^2\varphi(r(ll')) , \quad (4.38)$$

where

$$D^3\varphi(r)=\frac{1}{r^3}\varphi'''(r)-\frac{3}{r^4}\varphi''(r)+\frac{3}{r^5}\varphi'(r) . \quad (4.39)$$

With these results in hand, we can rewrite $F_\gamma(l''\,|\,T)$ [Eq. (3.32)] and $F_{\gamma\nu}(T)$ [Eqs. (4.21) and (4.22)] in the following forms:

$$F_\gamma(l''\,|\,T)=\tfrac{1}{2}\sum_{\alpha\beta}\sum_{l(\neq l'')}[-\langle u_\alpha(l'')u_\beta(l'')\rangle-\langle u_\alpha(l)u_\beta(l)\rangle$$

$$+\langle u_\alpha(l)u_\beta(l'')\rangle+\langle u_\alpha(l'')u_\beta(l)\rangle]\,\varphi_{\alpha\beta\gamma}(ll'') , \quad (4.40)$$

$$F_{\gamma\nu}(T)=\tfrac{1}{2}\sum_{\alpha\beta}\sum_{l(\neq l'')}\sum_{l''}[\langle u_\alpha(l)u_\beta(l)\rangle-\langle u_\alpha(l)u_\beta(l'')\rangle]$$

$$\times\varphi_{\alpha\beta\gamma}(ll'')\,x_\nu(ll'') . \quad (4.41)$$

For a slab of a cubic crystal bounded by (001) free surfaces, we know from Eqs. (4.9) and (4.22) that

$$F_\gamma(l''\,|\,T)=\delta_{\alpha z}F_z(l_3\,|\,T) , \quad (4.40')$$

$$F_{\gamma\nu}(T)=\delta_{\gamma\nu}F_B(T)+O(N_s/N_a) . \quad (4.41')$$

2. *bcc-Crystal Model*

We will use the same model as Clark *et al.*[9] for a monatomic bcc lattice. Each particle of the lattice is assumed to interact with its nearest and next-nearest neighbors. In the bulk, the equation of motion for the x component of the atom identified by the all-even or all-odd integers (l, m, n) can be written in the harmonic approximation as

$$M\ddot{u}_x(l,m,n)=\alpha_1\sum_{\lambda\mu\nu=\pm1}[u_x(l+\lambda,\ m+\mu,\ n+\nu)-u_x(l,m,n)]$$

$$+\alpha_2\sum_{\lambda\mu\nu=\pm1}[\lambda\mu u_y(l+\lambda,m+\mu,n+\nu)+\lambda\nu u_z(l+\lambda,m+\mu,n+\nu)]$$

$$+\beta_1\sum_{\lambda=\pm2}[u_x(l+\lambda,m,n)-u_x(l,m,n)]+\beta_2\sum_{\lambda=\pm2}[u_x(l,m+\lambda,n)+u_x(l,m,n+\lambda)-2u_x(l,m,n)] . \quad (4.42)$$

Corresponding equations for $\ddot{u}_y(l, m, n)$ and $\ddot{u}_z(l, m, n)$ can be obtained from Eq. (4.42) by suitable permutations of symbols.

Using (4.13) and (4.33), we can evaluate the matrix $\underline{\overline{\Phi}}_{zz}$ in the bulk. Let us simplify our notation and use

$$\overline{\Phi}_{zz}(l_3, l_3')\equiv -L_{nm} , \quad l_3\equiv n, \quad l_3'\equiv m . \quad (4.43)$$

The nonzero elements of this matrix for this model are

$$L_{mm}=-8\alpha_1-2\beta_1 ,$$

$$L_{m,m+1}=L_{m+1,m}=4\alpha_1 , \quad (4.44)$$

$$L_{m,m+2}=L_{m+2,m}=\beta_1 .$$

We need to calculate the inverse $\underline{G}$ of $\underline{L}$:

$$\underline{L}\,\underline{G}=\underline{I} . \quad (4.45)$$

To obtain $\underline{G}$, we use the Fourier transform

$$G_{mn}=G(m-n)=\int_{-\pi}^{+\pi}e^{i(m-n)\varphi}\,g(\varphi)\,d\varphi . \quad (4.46)$$

We obtain in this way

$$g(\varphi)=1/2\pi\omega(\varphi) , \quad (4.47)$$

where

$$\omega(\varphi)=8\alpha_1[\cos(\varphi)-1]+2\beta_1[\cos(2\varphi)-1] . \quad (4.48)$$

By creating from an infinite crystal a slab between $n=0$ and $n=N$, by the cutting procedure described above, the matrix $\underline{L}$ will be modified by a matrix $\delta\underline{L}$,

$$\underline{L}'=\underline{L}-\delta\underline{L} . \quad (4.49)$$

For the slab studied here

$$\delta\underline{L}=\begin{pmatrix}\delta\underline{L}_0 & 0\\ 0 & \delta\underline{L}_N\end{pmatrix} . \quad (4.50)$$

$\delta\underline{L}_0$ and $\delta\underline{L}_N$ are 4×4 matrices connecting, respectively, $n=1$, 0, -1, and -2, and $n=N+2$, $N+1$, N, $N-1$. We have

$$\delta\underline{L}_0=\delta\underline{L}_N=-\begin{pmatrix}\beta_1 & 0 & -\beta_1 & 0\\ 0 & 4\alpha_1+\beta_1 & -4\alpha_1 & -\beta_1\\ -\beta_1 & -4\alpha_1 & 4\alpha_1+\beta_1 & 0\\ 0 & -\beta_1 & 0 & \beta_1\end{pmatrix} . \quad (4.51)$$

The inverse of $\underline{L}'$ is defined by

$$\underline{U}\,\underline{L}'=\underline{I} . \quad (4.52)$$

We simplify our notation by writing

$$P_n = -P_z(l_3)\ ,$$
$$w(n) = d_z(l_3)\ , \quad l_3 \equiv n\ . \tag{4.53}$$

With these notations, Eqs. (4.14) and (4.16) read

$$\sum_m L'_{nm}\, w(m) = P_n\ , \tag{4.54a}$$

$$w(m) = \sum_{n=0}^{N} U_{mn} P_n\ . \tag{4.54b}$$

Let us remark that by summing on n the right-hand side of Eq. (4.54a), we obtain for a slab a useful relation:

$$\sum_{n=0}^{N} P_n = 0\ . \tag{4.55}$$

$\underline{U}$ can be calculated from the Dyson relation:

$$\underline{U} = \underline{G} + \underline{U}\ \delta \underline{L}\,\underline{G}\ . \tag{4.56}$$

From there, we can now obtain (Appendix A) the dynamical displacements $w(m)$,

$$w(m) = \frac{1}{4(\alpha_1 + \beta_1)} \left((m - \tfrac{1}{2}N) \sum_{n=0}^{N_0} P_n + \sum_{n=m}^{N_0} |n - m|\, P_n + \frac{t}{1-t^2} \sum_{n=0}^{N} t^{|m-n|} P_n + \frac{K}{1-t^2}\,(t^{m+1} - t^{N+1-m}) \right), \tag{4.57}$$

where

$$N_0 = \begin{cases} \tfrac{1}{2}N & \text{for } N \text{ even} \\ \tfrac{1}{2}(N-1) & \text{for } N \text{ odd}\ , \end{cases} \tag{4.58}$$

$$t = (b^2 - 1)^{1/2} - b\ , \tag{4.59}$$

$$b = 1 + 2\alpha_1/\beta_1\ , \tag{4.60}$$

$$K = \sum_{n=0}^{N} t^n P_n\ . \tag{4.61}$$

We have neglected in (4.57) terms proportional to t^N going to zero when N is going to infinity. We also used the antisymmetry of the forces P_n through the middle of the slab, $P_n = -P_{N-n}$. One sees also that the solution (4.57) has the following property:

$$w(m) = -w(N - m)\ , \tag{4.62}$$

as could be expected by symmetry.

Let us note that the first term in (4.57) describes a homogeneous expansion of the slab due to its free surfaces. As indicated in Eqs. (4.17) and (4.28), we will add this term to ϵ_{zz} given by Eq. (4.26b) and get Eq. (4.28):

$$\hat{\epsilon}_{zz} = \epsilon_{zz} + \frac{1}{4(\alpha_1 + \beta_1)}\ \frac{2}{a} \sum_{n=0}^{N_0} P_n\ , \tag{4.63}$$

where $\frac{1}{2}a$ is the distance between the layers.

In this way, we are left with the part of $w(m)$ decaying to zero, with increasing distance from the free surfaces. Let us call it $w_s(m)$:

$$w_s(m) = \frac{1}{4(\alpha_1 + \beta_1)} \left(\sum_{n=m}^{N_0} |n - m|\, P_n + \frac{t}{1-t^2} \sum_{n=0}^{N} t^{|m-n|} P_n + \frac{K}{1-t^2}\,(t^{m+1} - t^{N+1-m}) \right). \tag{4.64}$$

In the following sections we will calculate the forces P_n and give an analytical result for $\epsilon_{xx} = \hat{\epsilon}_{zz}$ in the case of a bcc slab bounded by (001) free surfaces.

3. Calculation of the Forces P_n

Using the model described above, we obtained for the $\Phi_z(l_3)$ given by Eqs. (4.30), (4.31), and (4.32),

$$\begin{aligned} \Phi_z(0) &= -[(4/\sqrt{3})\,\varphi'(r_0) + \varphi'(2r_0/\sqrt{3})] \\ &= 2a(\alpha_2 - \alpha_1) - a\beta_2\ , \\ \Phi_z(1) &= -\varphi'\,(2r_0/\sqrt{3}) = -a\beta_2\ , \\ \Phi_z(N) &= -\Phi_z(0)\ , \qquad \Phi_z(N-1) = -\Phi_z(1)\ , \\ \Phi_z(n) &= 0 \qquad \text{for } 1 < n < N-1\ . \end{aligned} \tag{4.65}$$

The $G_{z\beta\beta}(l_3)$ are obtained from their definition (4.4) to be, in this model,

$$\begin{aligned} G_{zzz}(0) &= \frac{4r_0}{3\sqrt{3}}\ \varphi''(r_0) + \frac{2r_0}{\sqrt{3}}\ \varphi''\left(\frac{2r_0}{\sqrt{3}}\right) + \frac{8}{3\sqrt{3}}\ \varphi'(r_0) \\ &= a(2\alpha_1 + \beta_1)\ , \\ G_{zzz}(1) &= a\,\varphi''(a) = a\,\beta_1\ , \\ G_{zxx}(0) &= \frac{4r_0}{3\sqrt{3}} \left(\varphi''(r_0) - \frac{\varphi'(r_0)}{r_0}\right) = 2a\alpha_2\ , \\ G_{zxx}(1) &= 0\ , \\ G_{z\beta\beta}(l_3) &= 0 \qquad \text{for } 1 < l_3 < N-1\ , \\ G_{z\beta\beta}(N) &= -G_{z\beta\beta}(0)\ , \\ G_{z\beta\beta}(N-1) &= -G_{z\beta\beta}(1)\ , \\ G_{zyy}(n) &= G_{zxx}(n)\ . \end{aligned} \tag{4.66}$$

We will obtain the forces P_n from Eqs. (4.53) and (4.11) and the above results, by estimating $\epsilon_{\beta\beta}$ and $F_z(l_3 \mid T)$ given by Eqs. (4.26) and (4.40). We need now to calculate $F_B(T)$ and $F_z(l_3 \mid T)$ from, respectively, Eqs. (4.41) and (4.40).

Let us define

$$R_{\alpha\beta}(ll') = \langle u_\alpha(l) u_\beta(l) \rangle - \langle u_\alpha(l) u_\beta(l') \rangle\ . \tag{4.67}$$

We will write in the bulk $R_{\alpha\beta}(ll') = R_{\alpha\beta}(r)$, where r is the distance between atoms l and l'.

Let us define

$$S_{\alpha\beta}(ll') = -[R_{\alpha\beta}(ll') + R_{\alpha\beta}(l'l)]\ . \tag{4.68}$$

For l in the nth plane parallel to the (001) surfaces, we define also

$$S_{\alpha\beta}^{(i)}(n)=S_{\alpha\beta}(ll')-S_{\alpha\beta}(ll'') , \qquad (4.69)$$

where $i=1$, when l' and l'' label a first-nearest neighbor of l situated, respectively, in planes $n+1$ and $n-1$; $i=2$ when l' and l'' label a second-nearest neighbor of l, respectively, in planes $n+2$ and $n-2$. When l' or l'' falls outside of the slab, the corresponding $S_{\alpha\beta}(ll')$ is zero in Eq. (4.69).

We can now obtain from Eqs. (4.40) and (4.41) in the central-force model of a bcc lattice described above

$$F_B(T)=N_a\left[\tfrac{4}{3}r_0 R_{\alpha\alpha}(r_0)\,\varphi'''(r_0)+aR_{\alpha\alpha}(a,\alpha)\,\varphi'''(a)\right] . \qquad (4.70)$$

In this expression $R_{\alpha\alpha}(a,\beta)=R_{\alpha\alpha}(ll')$, where l' labels a second-nearest neighbor of l situated on the β axis. We obtain also

$$F_z(n\,|\,T)=\frac{2}{3\sqrt{3}}\,S_{zz}^{(1)}(n)\left(\varphi'''(r_0)+6\,\frac{\varphi''(r_0)}{r_0}-6\,\frac{\varphi'(r_0)}{r_0^2}\right)+\frac{4}{3\sqrt{3}}\,S_{xx}^{(1)}(n)\,\varphi'''(r_0)+\tfrac{1}{2}S_{zz}^{(2)}(n)\,\varphi'''(a)+S_{xx}^{(2)}(n)\left(\frac{\varphi''(a)}{a}-\frac{\varphi'(a)}{a^2}\right) . \qquad (4.71)$$

From Eqs. (4.26) and (4.70), we now obtain

$$\epsilon_{xx}(T)=\frac{2}{a^2(C_{11}+2C_{12})}\left(\frac{2}{\sqrt{3}}\,\varphi'''(r_0)R_{xx}(r_0)+\varphi'''(a)R_{xx}(a,x)\right) , \qquad (4.72)$$

$$\hat{\epsilon}_{zz}(T)=\epsilon_{xx}(T)+O(N_s/N_a). \qquad (4.73)$$

To obtain an order-of-magnitude estimate of the effects studied here, we will now apply the preceding results to a particular crystal mode. Numerical results will be given for a slab of α-iron, bounded by (001) free surfaces.

V. APPLICATION TO A PARTICULAR CRYSTAL MODEL

We will now describe an easy and approximate way to obtain numerical values for the correlation functions $\langle u_\alpha(l)u_\beta(l')\rangle$. Then we will choose a Lennard-Jones interatomic potential, in order to obtain numerical values of the "anharmonic" derivatives φ'''. Finally numerical results for the thermal expansion of a slab of α-iron bounded by (001) free surfaces will be given.

A. Calculation of Correlation Functions

To evaluate the ϵ_{xx}, $\hat{\epsilon}_{zz}$, and $w_s(m)$ obtained in Sec. IV, Eqs. (4.72), (4.73), and (4.64), we have to calculate the $\{R_{\alpha\beta}(ll')\}$, Eq. (4.67), and therefore the correlation functions[1] [Eq. (3.29)]

$$\langle u_\alpha(l)u_\beta(l')\rangle=(\hbar/2M)\left[\underline{D}^{-1/2}\coth(\tfrac{1}{2}\beta\hbar\underline{D}^{1/2})\right]_{l\alpha,l'\beta} . \qquad (5.1)$$

We will rewrite the dynamical matrix as

$$\underline{D}=\underline{d}+\underline{R} , \qquad (5.2)$$

where $\underline{d}$ is the diagonal part of $\underline{D}$ and $\underline{R}$ is the remainder. We will use Schafroth's expansion[14] near the diagonal $\underline{d}$ of a function $G_0(\underline{d}+\underline{R})$ in which $\underline{R}$ is small in comparison to $\underline{d}$.

Let us call p the symbols $\overline{(l,\alpha)}$, for simplicity, and define

$$d_{pp}=\lambda(p) , \qquad (5.3a)$$

with

$$\lambda\equiv\lambda(p) , \quad \lambda'\equiv\lambda(p') , \ldots , \quad \lambda_i\equiv\lambda(p_i) \qquad (5.3b)$$

and

$$G_n(\lambda_0,\lambda_1,\ldots,\lambda_n)=\sum_{i=0}^{n}\left(G_0(\lambda_i)\Big/\prod_{j\neq i}(\lambda_i-\lambda_j)\right) , \qquad (5.4)$$

which has the following property:

$$\lim_{\lambda_1\to\lambda_0,\lambda_2\to\lambda_0,\ldots,\lambda_m\to\lambda_0} G_n(\lambda_0,\lambda_1,\ldots,\lambda_n)=\frac{1}{m!}\,\frac{\partial^m}{\partial\lambda_0^m}\,G_{n-m}(\lambda_0,\lambda_{m+1},\ldots,\lambda_n) . \qquad (5.5)$$

With these notations, Schafroth's expansion[14] is

$$\left|G_0(\underline{D})\right|_{p,p'}=I_{pp'}\,G_0(\lambda)+R_{pp'}\,G_1(\lambda,\lambda')+\sum_{n=2}^{\infty}\sum_{p_1\cdots p_{n-1}}R_{pp_1}R_{p_1p_2}\cdots R_{p_{n-1}p'}\times G_n(\lambda,\lambda_1,\ldots,\lambda_{n-1},\lambda') , \qquad (5.6)$$

where $\underline{I}$ is the identity matrix. Using Eq. (5.5), it is easy to see that Schafroth's expansion is equivalent to Taylor's if

$$\lambda(p)\equiv\lambda(p') ,$$

which is the case for infinite crystals.

This kind of expansion was used previously[15–20] and was shown on simple models[16–18] to give results approaching the exact values obtained by more complicated calculations, with precisions comparable to the experimental ones, when retaining only the first two correction terms in the expansion (5.6). In Refs. 17–20a, Taylor's expansion was used rather than Schafroth's. This was found to give errors of the order of 2% for the mean-square displacements of surface atoms.[20b]

In Appendix B we give the $\langle u_\alpha(l)u_\beta(l')\rangle$ we need to obtain the ϵ_{xx}, $\hat{\epsilon}_{zz}$, and $w_s(m)$ [Eqs. (4.72), (4.73), and (4.64)] expanded to second order in $\underline{R}$.

B. Choice of an Interatomic Potential

Following Clark *et al.*[9] we assume for the interatomic potential an expression of the Lennard-Jones type:

$$\varphi(r_1)=A_1/r_1^{12}-B_1/r_1^{6} , \qquad (5.7)$$

$$\varphi(r_2)=A_2/r_2^{12}-B_2/r_2^6\ , \tag{5.8}$$

where the subscripts 1 and 2 refer to nearest- and next-nearest-neighbor interactions, respectively, and r_i is the distance between the interacting particles: $r_1=r_0$ for first neighbors and $r_2=a=2r_0/\sqrt{3}$ for second neighbors. It is well known that α-Fe is not a Lennard-Jones crystal. Nevertheless, the qualitative results and the order of magnitude of the results given by this model are reliable. Our aim here is only to discuss qualitative results and order of magnitude. We also used a Morse potential to derive the results of this paper, and the numerical values were about the same. Let us note also that in the model of Clark *et al.*[9] the φ' and φ'' are independent of the choice of a potential. Only the "anharmonic" derivatives φ''' are a little different if one chooses a Lennard-Jones rather than a Morse potential.

The bulk equilibrium condition $\partial\Phi/\partial r\,|_{r=r_0}$ gives[9] the condition

$$4\varphi'(r_0)=-2\sqrt{3}\ \varphi'(2r_0/\sqrt{3})\ , \tag{5.9}$$

where primes denote derivatives with respect to the argument.

We have also[9] the following relations for the force constants:

$$\begin{aligned}
\alpha_1&=\varphi_{xx}(\tfrac{1}{2}a,\tfrac{1}{2}a,\tfrac{1}{2}a)=\tfrac{1}{3}[\varphi''(r_0)+(2/r_0)\,\varphi'(r_0)]\ ,\\
\alpha_2&=\varphi_{xy}(\tfrac{1}{2}a,\tfrac{1}{2}a,\tfrac{1}{2}a)=\tfrac{1}{3}[\varphi''(r_0)-(1/r_0)\,\varphi'(r_0)]\ ,\\
\beta_1&=\varphi_{zz}(0,0,a)=\varphi''(a)\ ,\\
\beta_2&=\varphi_{xx}(0,0,a)=\varphi'(a)/a\ .
\end{aligned}\tag{5.10}$$

These force constants can be related to the elastic constants c_{11}, c_{12}, c_{44} in the usual straightforward manner[21] by considering the continuum limit of Eq. (4.42). These results are[9]

$$ac_{11}=2(\alpha_1+\beta_1)\ ,\qquad ac_{12}=2\alpha_2\ ,\qquad ac_{44}=2\alpha_2\ . \tag{5.11}$$

We use here $\alpha_2=\frac{1}{2}a(c_{12}+c_{44})$. The fourth relation required to specify these parameters is obtained from the phonon bulk frequency,

$$\omega(\pi,0,0)=4(\alpha_1/M)^{1/2}\ . \tag{5.12}$$

To obtain numerical values of the anharmonic force constants and only for this purpose, we use the Lennard-Jones potentials, Eqs. (5.7) and (5.8), and obtain

$$\begin{aligned}
\varphi'''(r_0)&=-\frac{12\times13\times14\,A_1'}{r_0}+\frac{6\times7\times8\,B_1'}{r_0}\ ,\\
\varphi'''(a)&=-\frac{12\times13\times14\,A_2'}{a}+\frac{6\times7\times8\,B_2'}{a}\ ,
\end{aligned}\tag{5.13}$$

where

$$\begin{aligned}
A_1'&=\tfrac{1}{72}\,[(7/r_0)\,\varphi'(r_0)+\varphi''(r_0)]\ ,\\
B_1'&=\tfrac{1}{36}\,[(13/r_0)\,\varphi'(r_0)+\varphi''(r_0)]\ ,\\
A_2'&=\tfrac{1}{72}\,[(7/a)\,\varphi'(a)+\varphi''(a)]\ ,\\
B_2'&=\tfrac{1}{36}\,[(13/a)\,\varphi'(a)+\varphi''(a)]\ .
\end{aligned}\tag{5.14}$$

C. Numerical Results for α-Iron

We have made an explicit calculation for α-iron. The elastic constants and phonon frequency, which are taken from the work of Low,[22] have the following values at 16 °C:

$$\begin{aligned}
c_{11}&=2.332\times10^{12}\ \text{dyn/cm}^2\ ,\\
c_{12}&=1.355\times10^{12}\ \text{dyn/cm}^2\ ,\\
c_{44}&=1.180\times10^{12}\ \text{dyn/cm}^2\ ,\\
\hbar\omega(\pi,0,0)&=0.035\ \text{eV}\ .
\end{aligned}\tag{5.15}$$

The value of the unit-cube edge a is taken to be[23]

$$a=2.866\ \text{Å}\ . \tag{5.16}$$

In Fig. 2 we give, as decimal fractions for the (001) surface of α-iron, the static displacements $(2/a)w_s(m)$ [Eq. (4.64)], and the dynamical ones at $T=0$ °K and at the Debye temperature T_D of α-iron ($k_BT_D=\hbar\omega_{\max}$). Here we have $T_D\simeq406$ °K. Our results for the static displacements agree with those obtained by Clark *et al.*[9] Let us remark that even at $T=0$ °K the dynamical displace-

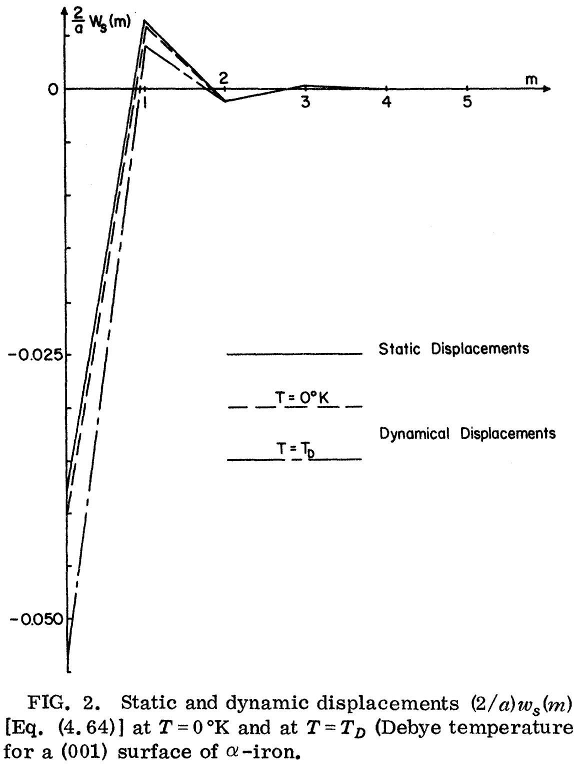

FIG. 2. Static and dynamic displacements $(2/a)w_s(m)$ [Eq. (4.64)] at $T=0$ °K and at $T=T_D$ (Debye temperature) for a (001) surface of α-iron.

ments are different from the static ones. This is due to the zero-point energy. We see that the surface layer is displaced outward. The displacements of successive layers are alternately outward and inward, and their magnitude approaches zero exponentially. It was checked that even a Morse potential gives the alternating character of the displacements $w_s(m)$. The uniformly outward static displacements obtained by Jackson[7b] for "α-Fe" may be due to the fact that his approach is a numerical one, and that we are considering only interactions between first and second neighbors. In Fig. 3, we give the variation with temperature of the dynamical displacements. In Fig. 4, we plotted as a function of temperature ϵ_{xx} [Eq. (4.72)].

In Fig. 5 we give the ratio between the surface and the bulk thermal expansion coefficients α_s/α_B. Let us define a_m as the spacing between the mth and the $(m-1)$th planes, and the thermal expansion coefficient between these planes as

$$\alpha_s(m) = a_m^{-1}\,\frac{\partial a_m}{\partial T}\ .$$

α_B is the value of $\alpha_s(m)$ in the bulk.

This surface thermal expansion was observed by Wilson *et al.*[24] on Mo and Cr at high temperature. At high temperatures, their simple interpretation

$$\alpha_s(1)/\alpha_B \simeq \langle u_z^2\rangle_1/\langle u_z^2\rangle_B$$

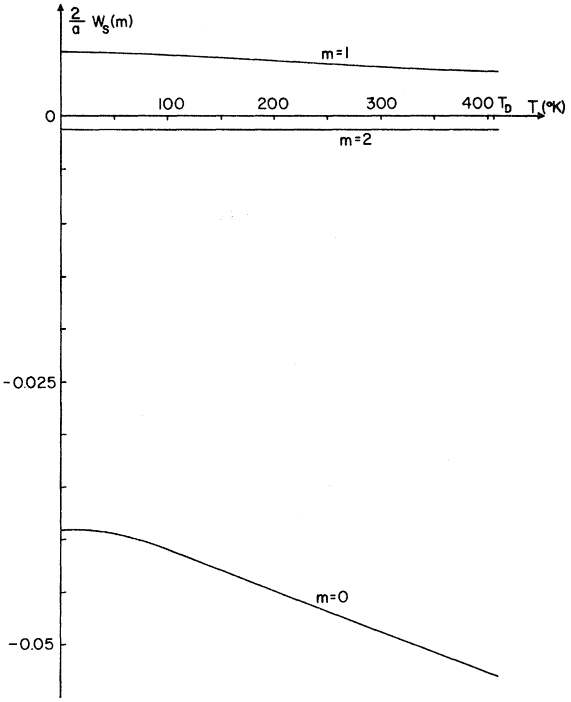

FIG. 3. Variation with temperature of the dynamic displacements $(2/a)w_s(m)$.

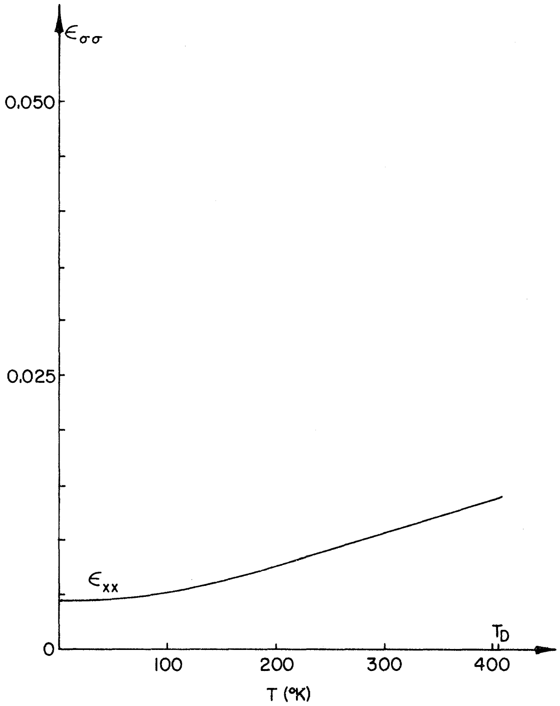

FIG. 4. Variation with temperature of strain parameter $\epsilon_{xx}=\hat{\epsilon}_{zz}$ [Eqs. (4.72) and (4.73)].

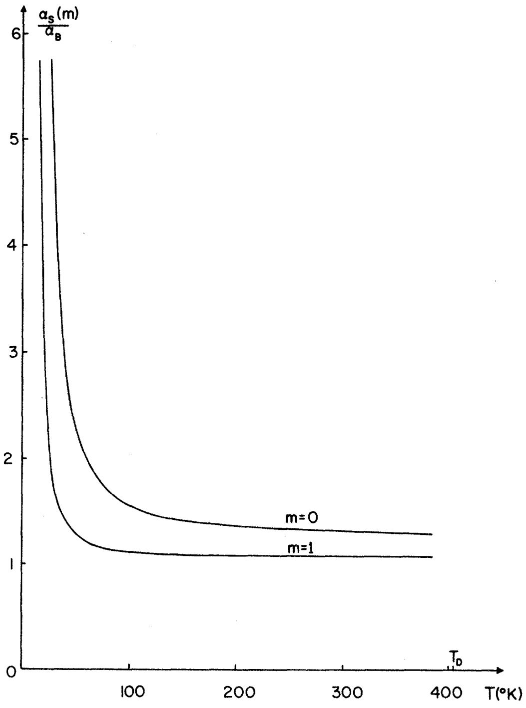

FIG. 5. Variation with temperature of the ratio between the thermal expansion coefficients $\alpha_s(m)$ near the surface and in the bulk.

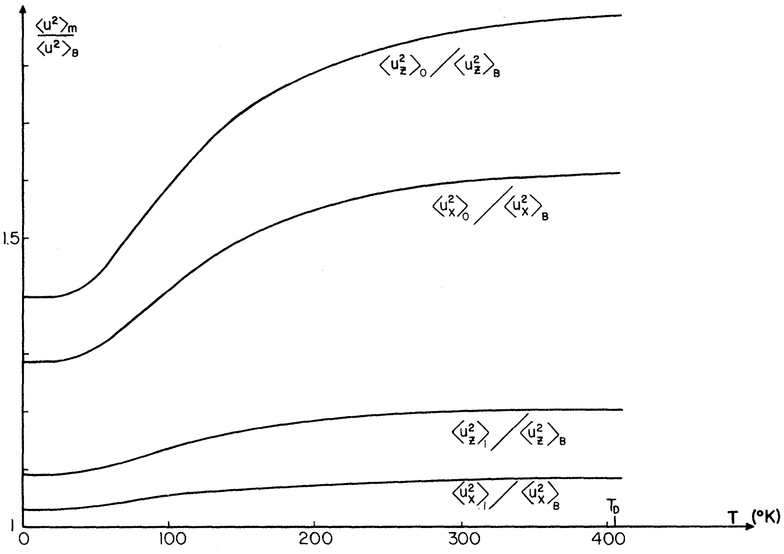

FIG. 6. Variation with temperature of the ratios of mean-square displacements for surface and bulk atoms.

seems accurate, as only orders of magnitude are taken into account. But in general, this relation is not so simple. The same comment can be made about the results obtained by Allen *et al.*[25,26]

Let us notice, also from Fig. 5, that at low temperatures, although $\alpha_s(1)$ as well as α_B is going to zero when T goes to zero, their ratio increases significantly. The bulk thermal expansion coefficient α_B obtained in this calculation is bigger by a factor of about 3 than the experimental one. This is due mainly to the fact that α-iron is not a Lennard-Jones crystal, and that the anharmonic force constants we used are too big. Therefore, we feel that the dynamical displacements reported here are also too big. Nevertheless, when ratios like α_s/α_B are considered, our results should be directly comparable to experimental values. Our aim here was mainly to discuss the different physical effects determining thermal expansion at a crystal surface.

In Fig. 6, we give the ratios between the mean-square displacements of bulk and surface atoms. Let us note that the difference between the mean-square displacements of atoms in layers 0 and 1 is quite important. In our calculation the mean-square displacements of atoms in layer 5 already have the bulk values. When measurements of mean-square displacements of surface atoms are reported by the low-energy-electron-diffraction (LEED) technique, it should therefore be made clear how far the low-energy electron penetrates into the crystal.

VI. CONCLUSIONS

We have presented in this paper a theory of the thermal expansion at a crystal surface which seems to be for the first time complete, analytical, and straightforward. This enabled us to discuss in a physical way the different effects involved: the static relaxation of the interplanar spacings in the vicinity of the crystal surface, the thermal expansion of the crystal arising from the cubic anharmonic terms in the crystal potential energy, and temperature-dependent changes in the interplanar spacings at the surface arising from the same source. Numerical estimates of these effects were presented for a slab of α-iron bounded by (001) faces.

LEED experiments[24] seem promising for the observation of surface thermal expansion.

ACKNOWLEDGMENTS

One of us (L. D.) would like to thank Professor R. F. Wallis, Professor D. L. Mills, and Dr. S. L. Cunningham for helpful discussions. He is also grateful to the National Science Foundation, the Centre National de la Recherche Scientifique, and the University of California, Irvine, for enabling him to spend one year in California as an Exchange Scientist.

APPENDIX A: SOLUTION FOR INTERPLANAR SPACINGS

Using Eqs. (4.50), (4.51), and (4.56) and the fact the $\underline{U}$ has the same block form as $\underline{L}'$ [Eq. (4.52)], which implies that $U_{mn} \equiv 0$ for m inside the slab and n outside, we obtain

$$U_{mn} = G(m-n) + \beta_1 U_{m1}[G(n+1) - G(n-1)] + \beta_1 U_{m,N-1}[G(N-n+1) - G(N-n-1)] + U_{m0}[4\alpha_1(G(n+1) - G(n)) + \beta_1(G(n+2) - G(n))] + U_{mN}[4\alpha_1(G(N-n+1) - G(N-n)) + \beta_1(G(N+2-n) - G(N-n))] . \quad (A1)$$

By rewriting $g(\varphi)$ from Eqs. (4.47) and (4.48) in the form

$$g(\varphi) = -\frac{1}{2\pi}\,\frac{1}{8(\alpha_1+\beta_1)}\left(\frac{1}{1-\cos\varphi}+\frac{1}{b+\cos\varphi}\right), \tag{A2}$$

where

$$b = 1 + 2\alpha_1/\beta_1 , \tag{A3}$$

we can calculate from (4.46)

$$G(n+1) - G(n) = \frac{1}{8(\alpha_1+\beta_1)}\left(\operatorname{sgn}(2n+1) + \frac{2t^{m+1}}{t+1}\right), \tag{A4}$$

where

$$t = (b^2-1)^{1/2} - b . \tag{A5}$$

The $w(m)$ given by Eq. (4.54b) may be expressed in the following form:

$$w(m) = \sum_{n=0}^{N} G(m-n)P_n + \frac{\beta_1 K}{4(\alpha_1+\beta_1)} \times(-U_{m1} + U_{m,N-1} + U_{m0} - U_{mN}) , \tag{A6}$$

where

$$K = \sum_{n=0}^{N} t^n P_n . \tag{A7}$$

To obtain (A6) we used (A4) and the fact that the P_n are antisymmetric through the middle plane of the slab,

$$P_n = -P_{N-n} ,$$

as well as the relation (4.55).

From (A1) we obtain directly, by using (A4) and neglecting terms proportional to t^N going to zero when $N\to\infty$,

$$2(\alpha_1+\beta_1)U_{m0} - (2\alpha_1+\beta_1)U_{mN} - \beta_1 U_{m,N-1} = 4(\alpha_1+\beta_1)G(m) , \tag{A8}$$

$$-2(\alpha_1+\beta_1)U_{m0} + (2\alpha_1+\beta_1)U_{m,N} - \beta_1 U_{m1} = 4(\alpha_1+\beta_1)G(N-m) . \tag{A9}$$

Let us now use the fact that for m inside the slab

$$U_{m,-1} = U_{m,N+1} = 0 ,$$

to obtain from (A1), with the help of (A4) and by neglecting terms proportional to t^N,

$$2\alpha_1\frac{(1-t)}{1+t}U_{m0} - (2\alpha_1+\beta_1)U_{m,N} + \beta_1(1-t)U_{m1} - \beta_1 U_{m,N-1} = 4(\alpha_1+\beta_1)G(m+1) , \tag{A10}$$

$$-2(\alpha_1+\beta_1)U_{m0} + 2\alpha_1\frac{(1-t)}{1+t}U_{m,N} - \beta_1 U_{m1} + \beta_1(1-t)U_{m,N-1} = 4(\alpha_1+\beta_1)G(N-m) . \tag{A11}$$

The set of four equations (A8)–(A11) and four unknowns reduce to a set of two equations [(A8) – (A10) – (A9) + (A11)] and [(A8) – (A9)] and two unknowns $[(U_{m,0}-U_{m,N}),\ (U_{m,1}-U_{m,N-1})]$, from which we can easily find

$$U_{m,0} - U_{m,N} - U_{m1} + U_{m,N-1} = \frac{4(\alpha_1+\beta_1)}{\beta_1(1-t)}\,[G(m) - G(m+1) + G(N-m+1) - G(N-m)] . \tag{A12}$$

Finally, by using (A4), (A6), and (A12), we have

$$w(m) = \sum_{n=0}^{N} G(m-n)P_n + \frac{K}{4(\alpha_1+\beta_1)(1-t^2)} \times (t^{m+1} - t^{N+1-m}) . \tag{A13}$$

Let us now write out explicitly the term

$$w_0(m) = \sum_{n=0}^{N} G(m-n)P_n . \tag{A14}$$

Using (4.46) and (A2), we have

$$w_0(m) = -\frac{1}{16\pi(\alpha_1+\beta_1)}\sum_{n=0}^{N}\left(\int_{-\pi}^{+\pi}\frac{\cos(m-n)\varphi}{1-\cos\varphi}\,d\varphi + \int_{-\pi}^{+\pi}\frac{\cos(m-n)\varphi}{b+\cos\varphi}\,d\varphi\right)P_n . \tag{A15a}$$

Using the relation (4.55), we can write

$$w_0(m) = -\frac{1}{16\pi(\alpha_1+\beta_1)} \times\sum_{n=0}^{N}\left(\int_{-\pi}^{+\pi}\frac{\cos(m-n)\varphi - \cos(m\varphi)}{1-\cos\varphi}\,d\varphi + \int_{-\pi}^{+\pi}\frac{\cos(m-n)\varphi}{b+\cos\varphi}\,d\varphi\right)P_n . \tag{A15b}$$

These integrals can be easily done and

$$w_0(m) = +\frac{1}{8(\alpha_1+\beta_1)}\left(\sum_{n=0}^{N}|n-m|P_n + \frac{2t}{1-t^2}\sum_{n=0}^{N}t^{|m-n|}P_n\right) . \tag{A16}$$

Let us now remark from Eqs. (A3) and (A5) that for N large

$$t^{|n|}\xrightarrow[m\to N/2]{} 0 , \qquad P_n \xrightarrow[n\to N/2]{} 0 . \tag{A17}$$

Let us define N_0 by

$$N_0 = \tfrac{1}{2}N \quad \text{for } N \text{ even}$$
$$= \tfrac{1}{2}N - \tfrac{1}{2} \quad \text{for } N \text{ odd} . \tag{A18}$$

This enables us to see from Eqs. (A13), (A14), and (A16) that

$$w(\tfrac{1}{2}N) = \frac{1}{8(\alpha_1+\beta_1)}\sum_{n=0}^{N}|n-\tfrac{1}{2}N|\,P_n . \tag{A19}$$

Now using again the antisymmetry of the P_n we have

$$\sum_{n=0}^{N} \left| n - \tfrac{1}{2}N \right| P_n = 0 \tag{A20}$$

and

$$w(\tfrac{1}{2}N) = 0 \ . \tag{A21}$$

This result could also be predicted from symmetry considerations.

Relations (A20) and (4.55) enable us to rewrite $w_0(m)$ in the form

$$w_0(m) = \frac{1}{4(\alpha_1+\beta_1)} \left((m - \tfrac{1}{2}N) \sum_{n=0}^{N_0} P_n + S(m) + \frac{t}{1-t^2} \sum_{n=0}^{N} t^{|m-n|} P_n \right) , \tag{A22}$$

where

$$S(m) = \sum_{n=m}^{N_0} (n-m) P_n \qquad \text{for } m < \tfrac{1}{2}N$$

$$= \sum_{n=N_0+1}^{m} (m-n) P_n \qquad \text{for } m > \tfrac{1}{2}N \ . \tag{A23}$$

$S(m)$ decays to zero when m goes away from the free surfaces. The contribution from terms involving n close to N_0 being negligible, we will write, in general,

$$S(m) = \sum_{n=m}^{N_0} |n-m| P_n , \tag{A24}$$

so that finally

$$w(m) = \frac{1}{4(\alpha_1+\beta_1)} \left((m - \tfrac{1}{2}N) \sum_{n=0}^{N_0} P_n + \sum_{n=m}^{N_0} |n-m| P_n + \frac{t}{1-t^2} \sum_{n=0}^{N} t^{|m-n|} P_n + \frac{K}{1-t^2} (t^{m+1} - t^{N+1-m}) \right) . \tag{A25}$$

APPENDIX B: CALCULATION OF CORRELATION FUNCTIONS $\langle u_\alpha(l) u_\beta(l') \rangle$

As explained in Sec. V [Eqs. (5.1)–(5.6)], we calculate here the correlation functions

$$\langle u_\alpha(l) u_\beta(l') \rangle = (\hbar/2M) [\underline{D}^{-1/2} \coth(\tfrac{1}{2}\beta\hbar \underline{D}^{1/2})]_{l\alpha, l'\beta} \tag{B1a}$$

$$= [G_0(\underline{D})]_{l\alpha, l'\beta} \tag{B1b}$$

using Schafroth's expansion[14] near the diagonal part $\underline{d}$ of the dynamical matrix:

$$\underline{D} = \underline{d} + \underline{R} \ . \tag{B2}$$

We will give here the first three terms of this expansion for the correlation functions we need to evaluate the $\{\epsilon_{\sigma\sigma}\}$ and the $\{d_z(l_3)\}$ for a slab of α-iron bounded by (001) free surfaces. We use the phonon model described in Sec. IV C 2. In what follows, we have $\beta = x$ or y.

In this model we have, with the notations (5.3),

$$\lambda_1 = d_{xx}(0,0) = (1/M)(4\alpha_1 + 2\beta_1 + 3\beta_2) ,$$

$$\lambda_2 = d_{zz}(0,0) = (1/M)(4\alpha_1 + \beta_1 + 4\beta_2) ,$$

$$\lambda_3 = d_{xx}(1,1) = (1/M)(8\alpha_1 + 2\beta_1 + 3\beta_2) ,$$

$$\lambda_4 = d_{zz}(1,1) = (1/M)(8\alpha_1 + \beta_1 + 4\beta_2) ,$$

$$\lambda_5 = d_{zz}(2,2) = d_{xx}(2,2) = (1/M)(8\alpha_1 + 2\beta_1 + 4\beta_2) \ . \tag{B3}$$

In $d_{\sigma\sigma}(n,n)$ the index n refers to the layer of the slab in which the atom we consider here is situated. Let us note that $d_{\sigma\sigma}(2,2)$ already has the bulk value.

The coefficients $G_n(\lambda_0, \lambda_1, \ldots, \lambda_n)$ [Eqs. (5.4) and (5.5)] we need here are

$$G_1(\lambda_i, \lambda_j) = \frac{G_0(\lambda_j) - G_0(\lambda_i)}{\lambda_j - \lambda_i} \qquad \text{for } i \neq j , \tag{B4}$$

$$G_2(\lambda_i, \lambda_j, \lambda_k) = \frac{G_0(\lambda_i)}{(\lambda_i - \lambda_j)(\lambda_i - \lambda_k)} + \frac{G_0(\lambda_j)}{(\lambda_j - \lambda_i)(\lambda_j - \lambda_k)} + \frac{G_0(\lambda_k)}{(\lambda_k - \lambda_i)(\lambda_k - \lambda_j)} \qquad \text{for } i \neq j \neq k \ . \tag{B5}$$

If we define

$$A_i = \tfrac{1}{2}\hbar \lambda_i^{1/2} / k_B T , \tag{B6}$$

we obtain

$$G_1(\lambda_i, \lambda_i) = -(\hbar/4M)(\lambda_i)^{-3/2} [\coth A_i + A_i \sinh^{-2} A_i] , \tag{B7}$$

$$G_2(\lambda_i, \lambda_i, \lambda_i) = (\hbar/16M)(\lambda_i)^{-5/2} [3 \coth A_i + 3 A_i \sinh^{-2}(A_i) + 2 A_i^2 \sinh^{-3} A_i \cosh A_i] , \tag{B8}$$

$$G_2(\lambda_i, \lambda_i, \lambda_j) = \frac{1}{\lambda_j - \lambda_i} \left(\frac{1}{\lambda_j - \lambda_i} [G_0(\lambda_j) - G_0(\lambda_i)] - G_1(\lambda_i, \lambda_i) \right) \qquad \text{for } i \neq j \ . \tag{B9}$$

The $\langle u_\alpha(l) u_\beta(l') \rangle$ for the slab with (001) surfaces is a function of only l_3 and l_3'. We will therefore write it as $\langle u_\alpha(l_3) u_\beta(l_3') \rangle$.

We now give to second order in $\underline{R}$ the correlation functions we need to calculate the $\{\epsilon_{\sigma\sigma}\}$ and the $\{d_z(l_3)\}$:

$$\langle u_\alpha^2(4) \rangle = G_0(\lambda_5) + (1/M^2)(8\alpha_1^2 + 2\beta_1^2 + 4\beta_2^2 + 16\alpha_2^2) \times G_2(\lambda_5, \lambda_5, \lambda_5) + \cdots , \qquad \alpha = x, y, \text{ or } z$$

$$\langle u_\alpha(4) u_\alpha(3) \rangle = (\alpha_1/M) G_1(\lambda_5, \lambda_5) + (2/M^2)\alpha_1(\beta_1 + 2\beta_2) \times G_2(\lambda_5, \lambda_5, \lambda_5) + \cdots , \qquad \alpha = x, y, \text{ or } z$$

$$\langle u_\beta(4) u_\beta(2) \rangle = (\beta_2/M) G_1(\lambda_5, \lambda_5) + (4/M^2)\alpha_1^2 G_2(\lambda_5, \lambda_5, \lambda_5) + \cdots , \qquad \beta = x \text{ or } y$$

$$\langle u_z(4) u_z(2) \rangle = (\beta_1/M) G_1(\lambda_5, \lambda_5) + (4/M^2)\alpha_1^2 G_2(\lambda_5, \lambda_5, \lambda_5) + \cdots \ .$$

In the model used here and to second order in R, the correlation functions given above assume their bulk values. Let us give now the correlation functions changed by the presence of the free surface at $l_3=0$:

$$\begin{aligned}\langle u_\beta^2(3)\rangle &= G_0(\lambda_5)+(1/M^2)(8\alpha_1^2+16\alpha_2^2+2\beta_1^2+3\beta_2^2)\\ &\quad\times G_2(\lambda_5,\lambda_5,\lambda_5)+(1/M^2)\beta_2^2G_2(\lambda_5,\lambda_3,\lambda_5)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z^2(3)\rangle &= G_0(\lambda_5)+(1/M^2)(8\alpha_1^2+16\alpha_2^2+\beta_1^2+4\beta_2^2)\\ &\quad\times G_2(\lambda_5,\lambda_5,\lambda_5)+(1/M^2)\beta_1^2G_2(\lambda_5,\lambda_4,\lambda_5)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta(3)u_\beta(2)\rangle &= (\alpha_1/M)G_1(\lambda_5,\lambda_5)+(1/M^2)\alpha_1(2\beta_1+3\beta_2)\\ &\quad\times G_2(\lambda_5,\lambda_5,\lambda_5)+(1/M^2)\alpha_1\beta_2G_2(\lambda_5,\lambda_3,\lambda_5)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z(3)u_z(2)\rangle &= (\alpha_1/M)G_1(\lambda_5,\lambda_5)+(1/M^2)\alpha_1(\beta_1+4\beta_2)\\ &\quad\times G_2(\lambda_5,\lambda_5,\lambda_5)+(1/M^2)\alpha_1\beta_1G_2(\lambda_5,\lambda_4,\lambda_5)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta(3)u_\beta(1)\rangle &= (\beta_2/M)G_1(\lambda_5,\lambda_3)\\ &\quad+(4/M_2)\alpha_1^2G_2(\lambda_5,\lambda_5,\lambda_3)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z(3)u_z(1)\rangle &= (\beta_1/M)G_1(\lambda_5,\lambda_4)\\ &\quad+(4\alpha_1^2/M^2)G_2(\lambda_5,\lambda_5,\lambda_4)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta^2(2)\rangle &= G_0(\lambda_5)+(1/M^2)(4\alpha_1^2+8\alpha_2^2+2\beta_1^2+3\beta_2^2)\\ &\quad\times G_2(\lambda_5,\lambda_5,\lambda_5)+(4/M^2)(\alpha_1^2+\alpha_2^2)G_2(\lambda_5,\lambda_3,\lambda_5)+(4/M^2)\\ &\quad\times\alpha_2^2G_2(\lambda_5,\lambda_4,\lambda_5)+(\beta_2^2/M^2)G_2(\lambda_5,\lambda_1,\lambda_5)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z^2(2)\rangle &= G_0(\lambda_5)+(1/M^2)(4\alpha_1^2+8\alpha_2^2+\beta_1^2+4\beta_2^2)\\ &\quad\times G_2(\lambda_5,\lambda_5,\lambda_5)+(8/M^2)\alpha_2^2G_2(\lambda_5,\lambda_3,\lambda_5)+(4/M^2)\\ &\quad\times\alpha_1^2G_2(\lambda_5,\lambda_4,\lambda_5)+(\beta_1^2/M^2)G_2(\lambda_5,\lambda_2,\lambda_5)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta(2)u_\beta(1)\rangle &= (\alpha_1/M)G_1(\lambda_5,\lambda_3)+(\alpha_1/M^2)\\ &\quad\times\beta_1G_2(\lambda_5,\lambda_1,\lambda_3)+(\alpha_1/M^2)(2\beta_2+\beta_1)G_2(\lambda_5,\lambda_5,\lambda_3)\\ &\quad+(\alpha_1/M^2)(\beta_1+\beta_2)G_2(\lambda_5,\lambda_3,\lambda_3)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z(2)u_z(1)\rangle &= (\alpha_1/M)G_1(\lambda_5,\lambda_4)+(\alpha_1/M^2)\\ &\quad\times\beta_1G_2(\lambda_5,\lambda_2,\lambda_4)+(\alpha_1/M^2)(2\beta_2+\beta_1)G_2(\lambda_5,\lambda_5,\lambda_4)\\ &\quad+(2/M^2)\alpha_1\beta_2G_2(\lambda_5,\lambda_4,\lambda_4)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta(2)u_\beta(0)\rangle &= (\beta_2/M)G_1(\lambda_5,\lambda_1)\\ &\quad+(4\alpha_1^2/M^2)G_2(\lambda_5,\lambda_3,\lambda_1)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z(2)u_z(0)\rangle &= (\beta_1/M)G_1(\lambda_5,\lambda_2)\\ &\quad+(4/M^2)\alpha_1^2G_2(\lambda_5,\lambda_4,\lambda_2)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta^2(1)\rangle &= G_0(\lambda_3)+(2/M^2)(\beta_1^2+\beta_2^2)G_2(\lambda_3,\lambda_3,\lambda_3)\\ &\quad+(1/M^2)(4\alpha_1^2+8\alpha_2^2+\beta_2^2)G_2(\lambda_3,\lambda_5,\lambda_3)\\ &\quad+(4/M^2)(\alpha_1^2+\alpha_2^2)G_2(\lambda_3,\lambda_1,\lambda_3)\\ &\quad+(4/M^2)\alpha_2^2G_2(\lambda_3,\lambda_2,\lambda_3)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z^2(1)\rangle &= G_0(\lambda_4)+(1/M^2)(4\alpha_1^2+8\alpha_2^2+\beta_1^2)G_2(\lambda_4,\lambda_5,\lambda_4)\\ &\quad+(8/M^2)\alpha_2^2G_2(\lambda_4,\lambda_1,\lambda_4)+(4/M^2)\alpha_1^2G_2(\lambda_4,\lambda_2,\lambda_4)\\ &\quad+(4/M^2)\beta_2^2G_2(\lambda_4,\lambda_4,\lambda_4)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta(1)u_\beta(0)\rangle &= (\alpha_1/M)G_1(\lambda_3,\lambda_1)+(\alpha_1\beta_2/M^2)\\ &\quad\times G_2(\lambda_3,\lambda_5,\lambda_1)+(\alpha_1/M^2)(\beta_1+\beta_2)G_2(\lambda_3,\lambda_3,\lambda_1)\\ &\quad+(\alpha_1/M^2)(\beta_1+\beta_2)G_2(\lambda_3,\lambda_1,\lambda_1)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z(1)u_z(0)\rangle &= (\alpha_1/M)G_1(\lambda_4,\lambda_2)\\ &\quad+(\alpha_1\beta_1/M^2)G_2(\lambda_4,\lambda_5,\lambda_2)\\ &\quad+(2\alpha_1/M^2)\beta_2[G_2(\lambda_4,\lambda_4,\lambda_2)+G_2(\lambda_4,\lambda_2,\lambda_2)]+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_\beta^2(0)\rangle &= G_0(\lambda_1)+(2/M^2)(\beta_1^2+\beta_2^2)G_2(\lambda_1,\lambda_1,\lambda_1)\\ &\quad+(4/M^2)(\alpha_1^2+\alpha_2^2)G_2(\lambda_1,\lambda_3,\lambda_1)+(4/M^2)\\ &\quad\times\alpha_2^2G_2(\lambda_1,\lambda_4,\lambda_1)+(\beta_2^2/M^2)G_2(\lambda_1,\lambda_5,\lambda_1)+\cdots,\end{aligned}$$

$$\begin{aligned}\langle u_z^2(0)\rangle &= G_0(\lambda_2)+(4/M^2)\beta_2^2G_2(\lambda_2,\lambda_2,\lambda_2)+(8/M^2)\\ &\quad\times\alpha_2^2G_2(\lambda_2,\lambda_3,\lambda_2)+(4/M^2)\alpha_1^2G_2(\lambda_2,\lambda_4,\lambda_2)\\ &\quad+(\beta_1^2/M^2)G_2(\lambda_2,\lambda_5,\lambda_2)+\cdots.\end{aligned}$$

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[*] Research supported in part by the Air Force Office of Scientific Research, Office of Aerospace Research, USAF, under Grant No. AFOSR 71-2018.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 4 15 FEBRUARY 1973

Thermal-Resistivity Anisotropy of Zinc and Cadmium

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(Received 31 July 1972)

The Mannari–Ziman–Baym theory has been used to calculate the phonon-limited thermal resistivity of hexagonal metals in the two symmetry directions. This calculation introduces an inelastic contribution peculiar to anisotropic metals. A numerical computation using empirical form factors and experimental phonon spectra shows that this term could explain the low-temperature behavior of zinc.

I. INTRODUCTION

Experimental measurements of the thermal resistivity of hexagonal metal single crystals show peculiar behavior for zinc in the low-temperature range: The curves for $W_\perp$ and $W_\parallel$ appear to intersect above 20 K.[1,2] This does not happen for cadmium,[1,3] nor for the electrical resistivities of both metals.[4] A complete calculation of this anisotropy should take into account the Fermi-surface distortion (together with the exact form of Bloch waves), realistic phonon spectra, and the geometry of the umklapp processes. Moreover, at low temperature one should allow for inelastic scattering. Such a calculation is obviously quite intricate. As a first approximation, we have used the Mannari–Ziman–Baym theory.[5–7] In this theory one has to take a spherical Fermi surface but all the other previously mentioned factors can be taken into account. In the case of zinc and cadmium, the electrons are known to be nearly free, and this approximation is reasonable for not too low temperatures. Besides, analogous calculations have already been made for the electrical resistivity in cubic[8] and hexagonal metals[9–11] and it has been shown that they give the right order of magnitude for the anisotropy of single crystals of zinc, magnesium, and cadmium.[11]

In Sec. II we derive the formula we have used for the phonon-limited thermal resistivity of hexagonal metals. In Sec. III we give the results of numerical computation for zinc and cadmium, and in Sec. IV we give some conclusions and discuss the validity of the method.

II. THERMAL-RESISTIVITY CALCULATION

The thermal resistivity is given by[12]

$$W=\frac{1}{2k_B}\left(\iint(\Phi_{\vec{K}}-\Phi_{\vec{K}'})^2 P(\vec{K},\vec{K}')\,d\vec{K}\,d\vec{K}' \Big/ \left|\int v_{\vec{K}}(\epsilon_K-\xi)\,\Phi_K\,\frac{\partial f^0}{\partial\epsilon_K}\,d\vec{K}\right|^2\right). \qquad (1)$$

The trial function $\Phi_{\vec{K}}$ is taken as $\Phi_{\vec{K}}=(\epsilon_K-\xi)\vec{K}\cdot\vec{u}$ ($\vec{u}$ being a unit vector along the thermal gradient). The transition probability is

$$P(\vec{K}',\vec{K})=\frac{\Omega_0^2}{\hbar}\int_{-\infty}^{+\infty} S(\vec{q},\omega)\,|V(q)|^2 f^0(\vec{K}) \times[1-f^0(\vec{K}')]\,\delta(\epsilon_{K'}-\epsilon_K-\hbar\omega)\,d\omega\ , \qquad (2)$$

where Ω_0 is the atomic volume, $\vec{q}=\vec{K}-\vec{K}'$ is the diffraction vector, $S(\vec{q},\omega)$ is the dynamical structure factor (less the Bragg contribution), and $V(q)$ is the pseudopotential form factor. With the hypothesis of a spherical Fermi surface, the integration in $\vec{K}'$ is done analytically (see the Appendix) with the result