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Lattice-statics approach to surface calculations in a monatomic lattice*

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The method of lattice statics has been used to obtain a general formalism for determining atomic relaxations near surfaces of any given orientation in monatomic fcc or bcc lattices. Numerical results have been obtained for (100), (110), and (111) surfaces for semi-infinite slabs of α-iron and for the (100) surface of a "modified" Cu lattice. For these high-symmetry directions the three-dimensional equilibrium equations reduce to one dimension and the atomic relaxations are entirely normal to the surface.

I. INTRODUCTION

Recent advances in low-energy-electron diffraction (LEED) and Auger spectroscopy have given rise to increased efforts to calculate, from a theoretical standpoint, the effects of surface forces on defects within a crystal as well as formation and migration energies of defects on the crystal surfaces.[1–4] Fundamental to the calculation of surface properties in any crystal is a knowledge of the relaxed positions of the atomic layers in the vicinity of the surface, since formation energies and interactions occurring near a surface will be modified by relative displacements between the atoms of the host lattice in the region. The methods of calculation by which atomic displacements near a surface may be obtained do not differ greatly in principle from those used to calculate atomic displacements in the vicinity of point defects in bulk crystals and may be generally placed in one of two categories; direct-space techniques and Green's-function techniques. In direct-space techniques, one sets up a "computer model" of the lattice composed of perhaps a few thousand atoms and having a surface of the proper orientation on one boundary. Assuming a reliable pairwise potential is available to represent the interactions between pairs of host atoms, the direct-space force equations for the crystallite can be written and, starting with the host atoms at perfect lattice separation distances, the atoms in the lattice can be relaxed by an iterative process until the net force on each atom is zero, or at least smaller than some specified tolerance. This is the approach used by Wynblatt and Gjostein in their calculations for migration and formation energies for surface defects in copper[3] and tungsten,[4] and by Bonneton and Drechsler in their calculation of atomic relaxations near a (112) surface in W, Mo, and Ta.[5] It is, in essence, also the method applied by Jackson[6] in investigating relaxations of atoms at high-symmetry surfaces in a number of fcc and bcc metals.

In the Green's-function techniques, such as the method of lattice statics, used is made of translational symmetry to divide an infinite lattice into a number of "supercells" each containing a defect surrounded by a large number, N, of host atoms. The $3N\times 3N$ direct-space force equations for the atoms in a supercell are then Fourier transformed to reciprocal space, resulting in a set of N 3×3 decoupled force equations. Each of these 3×3 matrix equations can be solved by a straightforward matrix inversion, and the atomic displacements can then be found by a back transformation to direct space. A comprehensive formalism for determining atomic displacements at crystal surfaces using Green's functions has been developed by Feuchtwang.[7] The Green's-function approach has also been employed by Corciovei, Croitoru, and Grecu[8] in an attempt to determine the general characteristics of atomic displacements near surfaces in a fcc lattice and was earlier used by Gazis and Wallis[9] in their discussion of the properties of defects near a "surface" in a one-dimensional chain.

The direct-space calculations have the advantage that all of the forces on each atom in the model crystallite can be evaluated explicitly from an interatomic potential, whereas the Fourier transformation used in the Green's-function techniques is only applicable in the harmonic approximation. However, the computer "models" used in the direct-space approach are cumbersome and the number and complexity of the equilibrium equations increases rapidly with the size of the model crystallite. Moreover, crystallite size can be of critical importance if a very-long-range potential, such as a Morse potential or a Coulomb potential is being used. On the other hand, the supercell used in the lattice-statics approach can be made extremely large; in fact, by converting the Fourier sums to integrals, the supercell boundaries can be removed to infinity. In addition, the symmetry of the reciprocal lattice can be used to decrease significantly the length of the computations necessary in the lattice-statics approach. The present paper represents an application of the lattice-statics formalism developed previously[10–12] to determine the displacements of layers of host atoms induced by the formation of surfaces in bcc and fcc semi-infinite lattices. The theoretical approach presented is similar to that developed by Feuchtwang[7] but is greatly simplified and lends itself more readily to practical computations. The present development differs from that of Feuchtwang in the conversion of Fourier-space sums to integrals to obtain the relaxations associated with a semi-infinite slab and in the use of a surface layer placed symmetrically in the supercell, rather than an actual removal of half of the lattice. Because of the high symmetry of the (100), (110), and (111) surfaces for which lattice-statics calculations have been done, the three-dimensional equilibrium equations become one dimensional for these cases. However, the general theory presented in Sec. II is applicable to any surface orientation.

In carrying out numerical calculations of atomic relaxations, it is vital to have available an interatomic potential that correctly describes the changes in force constants which must occur during the formation of a surface. Unfortunately, the only potentials available currently for metals are intended to reflect the properties of the bulk material and cannot be expected to represent the changes brought about by the redistribution of valence electrons in the vicinity of a surface of a metal crystal. Nevertheless, some numerical calculations are presented in this paper using a bulk potential for α-iron in order to demonstrate, in a general way, the *type* of results one might obtain for high-symmetry surfaces in a bcc lattice. Difficulty was encountered in attemption to perform a similar set of calculations for a fcc metal such as Cu or Ni. The short-range potentials currently available for these materials give rise to nearest-neighbor force constants which are quite large compared to those of more distant neighbors. In attempting to use these potentials in the type of surface calculations described here, one encounters atomic relaxations which are much too large to be treated in the harmonic approximation. A calculation has been included in this paper which makes use of a set of force constants for Cu which have been "modified" to reduce the forces on the first two layers of atoms near the (100) surface, again, simply to demonstrate the application of the lattice statics equations to a specific case for a fcc lattice. None of the numerical results presented are intended to describe any actual surface properties.

Finally, emphasis is placed, in this paper, on the development of a purely lattice-statics approach to treating surface relaxations, and anharmonic effects have therefore been neglected completely. Anharmonic contributions could, in principle, be handled by applying the modified lattice-statics approach described in a previous paper.[13] This work is presently under way.

The general lattice-statics theory and its application to surfaces is presented in Sec. II. Section III is a description of the calculations carried out for the (100), (110), and (111) surfaces for α-iron, and the (100) surface of the "modified" Cu lattice. Section IV is a discussion of the results of those calculations, and Sec. V consists of a general summary of the work presented in this paper.

II. GENERAL THEORY

The method of lattice statics as applied to screw dislocations and to point defects in bulk crystals has been discussed fully elsewhere[10–12]; hence only a brief outline of the technique will be given here. The first step in this type of calculation is the application of periodic boundary conditions by subdividing the lattice into an infinite number of "supercells" each containing a large number, N, of host atoms with a defect at the center of the supercell. It is assumed that the interatomic interactions in the lattice can be described by means of a pairwise potential, $\phi(r)$. In the harmonic approximation, the direct-space force equations can be expressed by

$$F_\alpha^l = \sum_{l'} \sum_\beta \Phi_{\alpha\beta}^{ll'} \xi_\beta^{l'} \quad , \tag{1}$$

where

$$F_\alpha^l = \frac{\delta\Psi(|\vec{r}^l + \vec{\xi}^l|)}{\delta\xi_\alpha^l} \tag{2}$$

represents the direct-space force on the lth atom due to the defect. $\vec{r}^l$ is the position vector of the lth atom in the perfect lattice, $\vec{\xi}$ is the displacement of the lth atom after it relaxes in the presence of the defect, and $\Phi_{\alpha\beta}^{ll'}$ is the $3N\times 3N$ direct-space force-constant matrix for the lattice. The indices α and β refer to components in a Cartesian coordinate system in the lattice. $\Psi(\vec{r})$ represents the interatomic bonds broken (or formed) in the creation of the defect.

The direct-space equations in Eq. (1) are not very useful because of their complexity. Hence, in the lattice statics approach the direct-space displacements $\vec{\xi}^l$ are replaced by a Fourier transformation to reciprocal space,

$$\vec{\xi}^l = \frac{1}{N} \sum_{\vec{q}} \vec{Q}^{\vec{q}} e^{i\vec{q}\cdot\vec{r}^l} \quad , \tag{3}$$

where the $\vec{Q}^{\vec{q}}$ represents the Fourier amplitudes of the direct-space displacements and the $\vec{q}$ are the N allowed wave vectors in the first Brillouin zone (FBZ) of the superlattice. This transformation results in a set of decoupled equilibrium equations in reciprocal space, which may be written

$$F_\alpha^{\vec{q}} = \sum_\beta V_{\alpha\beta}^{-\vec{q}} Q_\beta^{\vec{q}} \qquad (4)$$

where the Fourier-transformed force array $\vec{F}^{\vec{q}}$ is

$$F_\alpha^{\vec{q}} = \sum_l F_\alpha^l e^{-i\vec{q}\cdot\vec{r}^l} \qquad (5)$$

and the reciprocal-space force-constant matrix $V_{\alpha\beta}^{-\vec{q}}$ is related to $\Phi_{\alpha\beta}^{ll'}$ by the expression

$$V_{\alpha\beta}^{-\vec{q}} = \sum_{l'} \Phi_{\alpha\beta}^{ll'} e^{-i\vec{q}\cdot\vec{r}^{l'}} . \qquad (6)$$

The Fourier amplitudes $\vec{Q}^{\vec{q}}$ can be obtained from Eq. (4) by direct matrix inversion and the direct-space displacements $\vec{\xi}^l$ can then be found by a back transformation to direct space as indicated in Eq. (3).

In applying a method of lattice statics to determine atomic relaxations near high-symmetry surfaces in fcc and bcc lattices the supercells are chosen to be parallelepipeds built up of N_l layers in the desired orientation, each containing the same number of atoms. The Cartesian coordinates for the supercell are chosen with the x and y axes in the plane of the layer at the middle of the supercell and the z axis is perpendicular to the planes formed by the layers. The analytic model of the surface is created by applying forces to the atoms on either side of the atomic layer at $z = 0$ in such a way as to cancel all interactions with the atoms in the $z = 0$ plane and all interactions extending across the $z = 0$ plane. Hence, if ρ is the interlayer spacing, the layers at $z = \pm\rho$ are surface planes. The entire lattice then resembles a continuum of slabs each having a thickness equal to the z dimension of a supercell.

It is important to note that the atoms in the $z = 0$ plane and the atomic bonds which cross that plane still contribute to the dynamical matrix $\vec{V}^{-\vec{q}}$. The presence of the surface (or any other defect in the lattice-statics formalism) is reflected entirely in the form of the force-array function $\vec{F}^{-\vec{q}}$, which contains contributions from all of the direct-space "external" forces which are applied to nullify the actual forces exerted between pairs of atoms whose bonds are altered in the formation of the surface.

The force array $\vec{F}^{\vec{q}}$ can be found by separately summing the x, y, and z components of the surface-induced forces exerted on each of the atoms in the $z = 1$ plane, the $z = 2$ plane, etc. as indicated in Eq. (5), and adding the results of the various sums. If the x and y components of the interatomic spacings in the lattice are assumed constant, it is not difficult to show that for the high-symmetry cases to be considered here, the x and y contributions of the external forces cancel completely so that the interaction between the "surface" and the atoms of the bulk crystal takes place only along the z direction.

The remaining $\vec{F}^{\vec{q}}$ component of the force array can be found by expressing the total surface-induced force on each atom in the $z = 1$ layer, and if necessary, on each atom in the $z = 2$ layers, $z = 3$ layer, etc. in terms of the first- and second-neighbor forces exerted by atoms in and beyond the surface layer and Fourier transforming these forces, again using Eq. (5). In so doing, one must sum over atoms on both sides of the $z = 0$ plane, i.e., atoms in the "phantom lattice" referred to by Gazis and Wallis.[9] If T_1 and T_2 are the total forces on atoms in the $z = 1$ and $z = 2$ layers, respectively, and ρ is the interlayer spacing in the z direction, for atoms in the first plane.

$$\begin{aligned}(F_z^{\vec{q}})_I &= T_1 e^{-iq_z\rho} \sum_l e^{-i(\vec{q}_\parallel\cdot\vec{r}_\parallel^l)} \\ &\quad - T_1 e^{iq_z\rho} \sum_l e^{-i(\vec{q}_\parallel\cdot\vec{r}_\parallel^l)} \\ &= -2iT_1 \sin(q_z\rho) \sum_l e^{-i(\vec{q}_\parallel\cdot\vec{r}_\parallel^l)} . \qquad (7)\end{aligned}$$

Following the same procedure for the remaining layers, one finds, in general, that

$$F_z^{\vec{q}} = -2i \sum_j T_j \sin(jq\rho) \sum_l e^{-i\vec{q}_\parallel\cdot\vec{r}_\parallel^l} , \qquad (8)$$

where $q_\parallel$ and $r_\parallel$ refer to components of the wave vectors and position vectors in the XY plane and j is summed over all layers of atoms having a direct interaction with the surface. Explicit expressions for the T_j in terms of interatomic forces depends upon the geometry of the surface and are given in Sec. III for the six cases considered there.

If one allows the supercell boundaries in the x and y directions to go to infinity, the direct-space sum over l becomes an integral,

$$\sum_l e^{-i\vec{q}_\parallel\cdot\vec{r}_\parallel^l} \to \int\int_{-\infty}^{\infty} \exp[-i(q_x r_x^l + q_y r_y^l)] \, dl_x \, dl_y \quad . \qquad (9)$$

Letting $\vec{r}_\parallel^l \equiv (a_x l_x, a_y l_y)$, Eq. (9) may be expressed as

$$\begin{aligned}\sum_l e^{-\vec{q}_\parallel\cdot\vec{r}_\parallel^l} &= [(2\pi)^2/a_x a_y] \\ &\quad \times \int_{-\infty}^{\infty}\int \exp[-i(q_x r_x^l + q_y r_y^l)] \, dr_x^l \, dr_y^l \quad , \qquad (10)\end{aligned}$$

where a_x and a_y are Cartesian components of the nearest-neighbor separation in the plane of the surface. The integral on the right-hand side of Eq. (10) is merely the definition of the Dirac δ function, $\delta(q_x, q_y)$. Hence, Eq. (8) can simply be written for the first- and second-neighbor *interlayer* forces

$$F_z^{\vec{q}} = \frac{-2i(T_1 \sin q_z\rho + T_2 \sin 2q_z\rho)(2\pi)^2 \delta(q_x, q_y)}{a_x a_y} . \qquad (11)$$

In order to determine the direct-space displacements, $\vec{\xi}^l$, using the force array given by Eq. (11) it is necessary to convert the wave-vector sum in Eq. (3) to an integral. Equation (3) then becomes

$$\xi_\alpha^l = \frac{Va}{(2\pi)^3} \int\int\int_{\mathrm{FBZ}} \vec{\mathrm{Q}}^{\vec{q}} e^{i\vec{q}\cdot\vec{r}^l} d^3q \quad , \tag{12}$$

where the integral is over the first Brillouin zone of the supercell. By choosing proper supercells in the form of rectangular parallelepipeds, the limits of the integrals are greatly simplified. However, the fact must be accounted for that the lattice symmetry, even for a set of coordinates that does not coincide with the [100] axes of the lattice, will not be simple tetragonal or orthorhombic, for example, but will be body-centered or face-centered tetragonal or orthorhombic. In order to properly account for the weighting of the wave vectors, the integral in Eq. (12) must be multiplied by an appropriate weighting index σ. The expression for ξ_α^l then becomes

$$\xi_\alpha^l = \frac{\sigma Va}{(2\pi)^3} \int\int\int_{-\pi}^{\pi} \vec{\mathrm{Q}}^{\vec{q}} e^{i\vec{q}\cdot\vec{r}^l} d^3q \tag{13}$$

The conversion of the wave-vector sums to integrals can be interpreted as increasing the supercell size to infinity so that the resulting atomic displacements are actually those for a semi-infinite slab.

The Fourier amplitudes $\vec{\mathrm{Q}}^{\vec{q}}$, obtained from the matrix inversion of Eq. (4) have three components;

$$\vec{\mathrm{Q}}^{\vec{q}} = [F_z^{\vec{q}}(V_{zx}^{-\vec{q}})^{-1}, F_z^{\vec{q}}(V_{zy}^{-\vec{q}})^{-1}, F_z^{\vec{q}}(V_{zz}^{-\vec{q}})^{-1}] \quad . \tag{14}$$

However, in each of the high-symmetry cases considered here, the expressions for $(V_{zx}^{-\vec{q}})^{-1}$ and $(V_{zy}^{-\vec{q}})^{-1}$ contain multipliers which become zero when the integrals over q_x or q_y are performed, because of the Dirac δ function in the force array. This means that for, at least, the (100), (110), and (111) surfaces in monatomic materials with cubic symmetry, there should be no tangential components of surface relaxation, a result which has been obtained more generally by Bonneton and Drechsler[5] and by Jackson.[6]

The final expression for the atomic displacements in the vicinity of a surface of high symmetry in a monatomic lattice with cubic symmetry is

$$\xi^l = \frac{\sigma Va(-2i)}{2\pi a_x a_y} \int\int\int (T_1 \sin q_z\rho + T_2 \sin 2q_z\rho) \times \delta(q_x, q_z)[V(q_x, q_y, q_z)]^{-1} e^{-i\vec{q}\cdot\vec{r}^l} d^3q \quad . \tag{15}$$

The δ function in the force array allows the x and y integrations to be performed immediately, resulting in a z integral, the evaluation of which depends only on wave vectors lying on the z axis:

$$\xi^l = \frac{\sigma Va}{2\pi a_x a_y} \int_{-\pi/\rho}^{\pi/\rho} (-2i) \times (T_1 \sin q_z\rho + T_2 \sin 2q_z\rho) \times [V(0, 0, q_z)]^{-1} e^{-iq_z\rho l} dq_z \quad , \tag{16}$$

where l may be regarded as indicating a given *layer* of atoms since ξ^l is obviously the same for all atoms in the same layer. For each of the high-symmetry surfaces in a monatomic lattice, except for the (111) surface in a bcc lattice, it can be shown that

$$[V(0, 0, q_z)]^{-1} = K_1(1 - \cos\rho q_z) + K_2(1 - \cos 2\rho q_z) \quad , \tag{17}$$

where K_1 and K_2 are functions of the radial and tangential force constants evaluated at first- and second-nearest-neighbor perfect lattice separations.

Equation (16) cannot be evaluated in closed form, but can be obtained by numerical techniques using a computer. The method used in the calculations discussed in Sec. III is the method of Gaussian quadratures which has been described in previous papers[11,12] and can be found in texts on numerical analysis. For simplicity, define $k_z = q_z\rho$. Then Eq. (16) becomes

$$\xi^l = \frac{\sigma Va}{2\pi a_x a_y \rho} \int_{-\pi}^{\pi} G(k_z) e^{-ik_z l} dk_z \tag{18}$$

where

$$G(k_z) = -2i(T_1 \sin k_z + T_2 \sin 2k_z) [V(0, 0, k_z)]^{-1} \,. \tag{19}$$

Using the method of Gaussian quadratures, the integral in Eq. (18) can now be obtained by evaluating the sum

$$\xi^l = \frac{\sigma Va}{2a_x a_y \rho} \sum_{n=1}^{M} G(\pi\mu_n) e^{-i\pi\mu_n} A(\mu_n) \quad , \tag{20}$$

where the μ_n are the zeroes of the Legendre polynomial of degree M.

The force constants which appear in $[V(0, 0, k_z)]^{-1}$ can be found from the pairwise interatomic potential $\phi(r)$ or from the elastic constants of the bulk crystal, but the interlayer forces T_1 and T_2 in the force array $F_z^{\vec{q}}$ are evaluated in the relaxed configuration of the lattice and are therefore functions of the relaxations of the first two or three layers below the surface. In the harmonic approximation the *interatomic* forces in the equilibrium configuration can be written as

$$\begin{aligned} F_1 &= \tfrac{1}{2} r^1 B_1 + \tfrac{1}{2} \xi_r^1 A_1 \quad , \\ F_2 &= \tfrac{1}{2} r^2 B_2 + \tfrac{1}{2} \xi_r^2 A_2 \quad , \end{aligned} \tag{21}$$

where ξ_r^1 and ξ_r^2 are the radial displacements of the first- and second-nearest-neighbor atoms, r^1 and r^2 are first- and second-neighbor separation distances in the perfect lattice, and A_i and B_i are defined as follows:

$$A_i \equiv 2 \frac{\delta^2\phi}{\delta r^2}\bigg|_{r_i} \quad , \quad B_i \equiv \frac{2}{r} \frac{\delta\phi}{\delta r}\bigg|_{r_i} \quad . \tag{22}$$

The interlayer forces can be expressed as func-

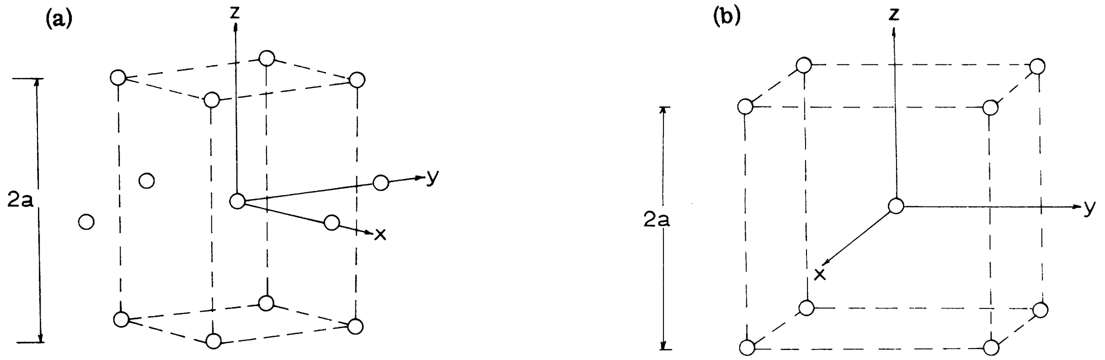

FIG. 1. (a) Body-centered tetragonal cell and coordinate system for (100) surface calculations in a fcc lattice. (b) Cubic cell used for (100) surface calculations in a bcc lattice.

tions of F_1 and F_2 and hence of ξ^1 and ξ^2 by proper consideration of the lattice geometry. Inserting these expressions into Eq. (20) one obtains a set of simultaneous equations in the displacements of the first and second layers of the surface which may be solved for ξ^1 and ξ^2. Once these displacements are known, T_1 and T_2 are fixed and the displacements of any of the remaining layers in the lattice may be found. A similar procedure may be followed for problems involving longer-range interlayer interactions.

Since Eq. (16) depends only on wave vectors lying on the z axis, it becomes apparent that the shape of the x and y supercell boundaries is really immaterial as long as one accounts properly for the number of atoms in each layer of the supercell. If the symmetry of the two-dimensional lattice in the xy plane is simple rectangonal (or simple cubic), then $a_x a_y$ is just the area per atom, A_a, in the layer and no correction need be made to the integral in Eq. (16). However, if the symmetry is area-centered rectangonal then $a_x a_y$ is only half of the area per atom, so that the wave vector sums or integrals over q_x and q_y will "count" twice as many wave vectors as actually exist and the integral in Eq. (16) must be divided by 2. In general, then, the weighting factor σ can be expressed as

$$\sigma = a_x a_y / A_a \quad . \tag{23}$$

III. APPLICATIONS

The general theory developed in the previous sections has been applied to six specific high-symmetry surface orientations in bcc and fcc monatomic lattices; the (100) surface, the (110) surface, and the (111) surface. In this section, the supercell configurations most suitable for numerical calculations for these six cases will be discussed and expressions for the T_i and K_i appearing in Eq. (15) and (16) will be given. Because of difficulties encountered in attempting to use bulk crystal force constants in a surface calculation, for "real" fcc lattices, numerical results are presented only for the bcc lattice using an α-iron potential developed by Johnson.[14] In order to present an example of the application of lattice statics to a (100) surface in a fcc metal and force constants for Cu described in an earlier paper[10] were modified to make them usable for surface calculations. The modification procedure will be discussed later.

The basic cubic cell for a fcc lattice is shown in Fig. 1(a). The Cartesian axes along the $\langle 100\rangle$ directions in the crystal would serve well as the coordinate system for (100) surface calculations. However, it is useful to rotate the system 45° about the z axis, as shown in Fig. 1(a), so that the two-dimensional matrix in the plane of the surface becomes a square with $a_x = \sqrt{2}a$ and $a_y = \sqrt{2}a$, where a is half the length of the cubic cell edge. The interlayer separation ρ in this case is equal to a. The supercell used for (100) surface calculations is built up of L^3 of these tetragonal cells and has dimensions $\sqrt{2}La \times \sqrt{2}La \times 2La$. Hence $a_x a_y = A_a$ and Eq. (20) becomes

$$\xi^l = \frac{1}{2}\sum_{n=1}^{m} G(\pi\mu_n)\, e^{-i\pi\mu_n^l} A(\mu_n) \quad . \tag{24}$$

The expressions for T_1, T_2, K_1, and K_2 for the (100) surface in a fcc lattice are

$$\begin{aligned} T_1 &= (2B_1 + B_2)\,a + (A_1 + A_2)\xi_z^1 \quad , \\ T_2 &= \mathrm{B}_2\, a + A_2 \xi_z^1 \quad , \\ K_1 &= 2(A_1 + B_1) \quad , \\ K_2 &= A_2 \quad . \end{aligned} \tag{25}$$

The basic unit cell for the bcc lattice is shown in Fig. 1(b), along with the Cartesian axes used for the (100) surface calculations. The supercell has dimensions $2La \times 2La \times 2La$ and contains $2L^3$ atoms.

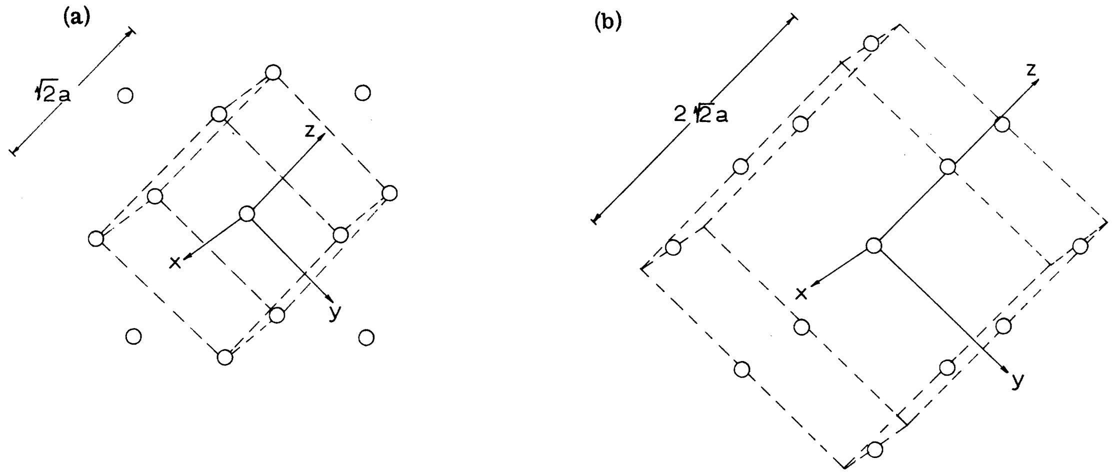

FIG. 2. (a) Body-centered tetragonal cell and Cartesian coordinates used for (110) surface calculations in a fcc lattice. (b) Face-centered orthorhombic cell and Cartesian coordinates used for (110) surface calculations in a fcc lattice.

Again, $a_x a_y = A_a$, and the coefficients of the displacement equations is therefore $\frac{1}{2}$, just as for the fcc case. T_1, T_2, K_1, and K_2 are

$$\begin{aligned} T_1 &= (2B_1 + B_2)\,a + (\tfrac{2}{3}A_1 + A_2)\,\xi_z^1 \quad , \\ T_2 &= B_2 a + \tfrac{1}{2}A_2 \xi_z^2 \quad , \\ K_1 &= \tfrac{4}{3}(A_1 + 2B_1) \quad , \\ K_2 &= A_2 \quad . \end{aligned} \tag{26}$$

The basic cell for calculating relaxations near a (110) surface in a fcc lattice is a body-centered tetragon, shown in Fig. 2(a). The supercell in this case has dimensions $2La \times \sqrt{2}La \times \sqrt{2}La$, containing L^3 atoms. Once more, $a_x a_y = A_a$ and $\sigma = 1$. Substituting these values into Eq. (20), one finds that the coefficients of the Gaussian sum is again $\frac{1}{2}$. For this case,

$$\begin{aligned} T_1 &= (\tfrac{3}{2}B_1 + 2B_2)\sqrt{2}\,a + (3A_1/2 + A_2)\xi_z^1 \quad , \\ T_2 &= (\tfrac{1}{2}B_1 + B_2)\sqrt{2}\,a + (A_1 + A_2)/2\,\xi_z^2 \quad , \\ K_1 &= A_1 + 3B_1 \quad , \\ K_2 &= A_1 + A_2 + B_2 \quad . \end{aligned} \tag{27}$$

The lattice cell used for (110) surface calculations for a bcc lattice is a face-centered tetragonal lattice, as shown in Fig. 2(b). The dimensions of the basic cell are $2a \times 2\sqrt{2}a \times 2\sqrt{2}a$ and the supercell, composed of L^3 basic cells has a volume of $16a^3$ and contains $4L^3$ atoms. Hence, σ in this case in $\frac{1}{2}$, since $a_x a_y = \frac{1}{2}A_a$. The coefficient of the Gaussian sum in Eq. (20) is again $\frac{1}{2}$. For this surface orientation, with only first- and second-neighbor atomic interactions there are no interactions across the surface boundary. The only bonds which must be "broken" are with two nearest neighbors and two next-nearest-neighbor atoms in the surface plane. $T_2 = 0$ and

$$\begin{aligned} T_1 &= (B_1 + B_2)\sqrt{2}\,a + (\tfrac{2}{3}A_1 + \tfrac{1}{2}A_2)\xi_z^1 \quad , \\ K_1 &= \tfrac{2}{3}(2A_1 + B_1) \quad , \\ K_2 &= A_2 + B_2 \quad . \end{aligned} \tag{28}$$

The coordinate system used in calculating atomic displacements at (111) surfaces in a fcc lattice is shown in Fig. 3(a). The dimensions of the basic cell used in this case are $\sqrt{2}a \times \sqrt{6}a \times 2\sqrt{3}a$. The supercell, made up of L^3 such cells has a volume $12a^3$ and contains $6L^3$ atoms. In the coordinate system given, $a_x a_y = \frac{1}{2}A_a$ and $\sigma = \frac{1}{2}$. Substituting these constants into Eq. (20) gives a coefficient of the Gaussian sum of $\frac{1}{2}$. As in the case of the (110) bcc surface the assumption of first- and second-neighbor atomic interaction means that there will be no interactions between atoms in the second layer and the "vacancy" layer at the $z = 0$ boundary. Hence T_2 is again zero. Atoms in the surface layer itself interact with three nearest neighbors and three next-nearest neighbors in the $z = 0$ plane. Again, there are no interatomic bonds extending across the surface boundary.

$$\begin{aligned} T_1 &= (B_1 + B_2)\sqrt{3}\,a + (A_1 + \tfrac{1}{2}A_2)\xi_z^1 \quad , \\ K_1 &= 2A_1 + B_1 \quad , \\ K_2 &= A_2 + B_2 \quad . \end{aligned} \tag{29}$$

The final case to be considered is that of the (111) surface in a bcc lattice. The basic cell for this case is shown in Fig. 3(b) and has dimensions $2\sqrt{2}a \times 2\sqrt{6}a \times \sqrt{3}a$. The supercell made up of L^3 such basic cells contains $6L^3$ atoms. Again, $a_x a_y = \frac{1}{2}A_a$, and the coefficient of the Gaussian sum in Eq. (20) is $\frac{1}{2}$, as it was for the fcc lattice. The (111) surface calculation for bcc lattices is com-

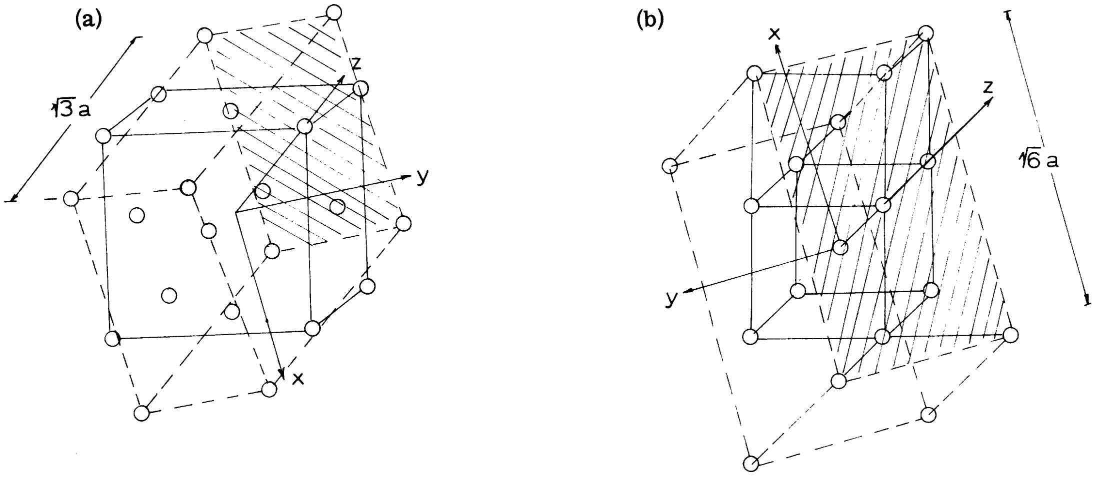

FIG. 3. (a) Orthorhombic cell and Cartesian coordinates used for (111) surface calculations in a fcc lattice. The top plane of the cell is shaded and certain edges of the cubic cell are shown by solid lines for reference. (b) Orthorhombic cell and Cartesian coordinates used for (111) surface calculations in a bcc lattice. The top plane of the cell is shaded and certain cubic cell edges are shown by solid lines for reference.

plicated by atomic interactions affecting the first three layers of atoms near the surface. Each atom in the first layer of the surface interacts with three atoms in the "vacancy" plane which are first-nearest neighbors and three second neighbors located in the first layer across the boundary at $z=0$, and finally, there is a direct "push" on a nearest-neighbor atom located in the *second* layer of atoms beyond $z=0$. The complete expression for T_1 is

$$T_1=\sqrt{3}a(B_1+B_2)+(\tfrac{2}{3}A_1+A_2)\xi_z^1+A_1/2\xi_z^2 \quad . \tag{30}$$

Each atom in the second layer of the surface interacts with one nearest-neighbor atom in the first layer across the boundary and three second-nearest neighbors in the vacancy plane at $z=0$. The resulting expression for T_2 is

$$T_2=\sqrt{3}a(B_1+\tfrac{1}{2}B_2)+A_2(1+1/\sqrt{3})/2\xi_z^2+A_2/2\xi_z^1 \quad . \tag{31}$$

Finally, each atom in the third layer interacts directly with one nearest-neighbor atom in the $z=0$ plane. Hence

$$T_3=\sqrt{3}a\,B_1/2+A_1/2\xi_z^3 \quad . \tag{32}$$

There is also an additional term $K_3(1-\cos 3kz)$ in the Fourier-inverted force-constant matrix, $(V^{-\vec{q}})^{-1}$. The constants K_1, K_2 and K_3 are

$$\begin{aligned} K_1&=(A_1+8B_1)/3 \quad ,\\ K_2&=A_2+2B_2 \quad ,\\ K_3&=A_1 \quad . \end{aligned} \tag{33}$$

Numerical calculations for the (100), (110), and (111) surfaces of α-iron have been carried out using the interatomic potential developed by Johnson.[14] No attempt was made to modify the potential to reflect actual physical changes near the surface, such as the redistribution of valence electrons. It was not necessary to use the explicit analytic expression for the potential in the surface calculations since the mathematical model of the surface involves breaking bonds only at perfect-lattice separations between atoms. Hence, only the first and second derivatives evaluated at perfect lattice positions are needed, and these are expressed as the force constants A_1, A_2, B_1 and B_2 [see Eq. (21)]. Numerical values of these constants are shown for α-iron in Table I.

Calculations were carried out to determine the relaxations of the first 20 layers of the surface in each case using a Legendre polynomial of order 40. The calculations were carried out partially on the IBM 360/65 at the University of Nebraska at Lincoln and partially using the KRONOS time-sharing system (CDC-6400) at the University of Nebraska at Omaha.

Numerical results for the first nine layers in the vicinity of the (100) surface of α-iron are shown in Table II. The relative displacements of the layers appear superimposed on a "uniform" displacement which occurs because the potential used gives rise to surfaces with nonzero forces on the first two layers. The atoms at the supercell boundaries are fixed; hence the atoms which interact directly with those in and across the $z=0$ plane relax until the unbalanced forces on them are zero. If the calculation were done with a fixed number of planes, the "uniform" relaxation would appear as an increase in lattice constant and would, in fact, be indistinguishable from the relative displacements.

TABLE I. Force-constant parameters for Cu and α-iron (dyn/cm).

	Cu	α-iron
A_1	6.6983×10^{4}	7.852343×10^{4}
A_2	-0.1118×10^{4}	3.143769×10^{4}
B_1	-0.5662×10^{4}	-0.394742×10^{4}
B_2	0.5662×10^{4}	0.394743×10^{4}

In the present case, however, there is an infinite number of atomic layers and this component of the relaxation appears as a uniform movement of the entire surface region.

The first- and second-neighbor radial force constants for α-iron are nearly equal and opposite, so that the sum of T_1 and T_2 before relaxation is very small, resulting in the extremely small displacement of the surface layer itself. The relative displacements display the alternate expansion and contraction characteristic of shells of atoms in the vicinity of single vacancies in bcc lattices.[13,14] The magnitudes of the relative displacements are seen to drop off rather rapidly for the first nine layers and beyond the ninth layer the uniform displacement is constant.

In the case of the (110) surface for α-iron, Eqs. (28) indicate that each atomic layer interacts only with the nearest-neighboring layers on each side. Hence, when the surface is formed each layer will exert a similar repulsion or attraction on its neighbors and only a uniform increase in lattice constant can result; there can be no "relative" displacements. Again, because $B_1 \simeq -B_2$, $T_1 \simeq 0$ in the unrelaxed position and the "uniform" displacement is very small; 3.07×10^{-5} Å toward the surface.

TABLE II. Relaxation of atomic layers near a (100) surface in α-iron (Å).

Layer	Displacement[a]	Relative displacement[b]
1	5.472×10^{-6}	+0.0948
2	−0.094833	−0.0198
3	−0.075019	+0.00414
4	−0.079159	−0.00086
5	−0.078294	+0.00018
6	−0.078474	−0.000037
7	−0.078437	+0.000008
8	−0.078445	−0.000002
9	−0.078443	

[a] Positive displacements are toward the surface.

[b] Positive signs denote relative expansion, negative signs denote relative contraction.

TABLE III. Relaxation of atomic layers near a (111) surface in α-iron (Å).

Layer	Displacement[a]	Relative displacement[b]
1	0.019445	+0.005712
2	0.013733	−0.011035
3	0.024768	+0.005549
4	0.019219	+0.00424
5	0.018795	−0.00244
6	0.021280	+0.00159
7	0.019690	−0.000147
8	0.019837	−0.000523
9	0.020360	+0.000435
10	0.019925	−0.000112
11	0.020037	−0.000097
12	0.020130	+0.000136
13	0.019994	−0.000016
14	0.020100	+0.000038

[a] Positive displacements are toward the surface.

[b] Positive signs denote relative expansion, negative signs denote relative contraction.

The numerical results for the displacements of the first 14 layers in the vicinity of the (111) surface in α-iron are given in Table III. Since there are interactions between first, second, and third layers, in this case neither the signs nor the magnitudes of the relative separations vary in any special pattern. It is interesting to note that relative compression between the second and third layers is larger in magnitude than the relative expansion between the surface layer and the layer next to the surface. The relative displacements appear to fall off more slowly with distance from the surface, reminiscent of the large displacement "spike" along the ⟨111⟩ direction associated with single vacancies in a bcc lattice.[13]

In attempting to perform a set of calculations for a standard fcc metal such as Cu, Ni, or Al, similar to those described for α-iron, it becomes apparent that the relaxations encountered (on the order of several angstroms) are meaningless in view of the harmonic approximation imposed. The difficulty in these cases is that the force constants associated with the interatomic potentials for the bulk crystal give rise to interactions between first-neighbor layers which are strongly repulsive and generally dominate the interactions between second-neighboring layers. This indicates that some drastic modifications in the force constants would probably be necessary in order to accurately represent the surfaces of such materials. Such modifications are beyond the scope of the present work, however, in the interest of presenting a numerical example of a lattice statics surface calculation for an fcc material, a set of force constants for copper, used in a previous calculation[15] were modified so that the radial force constants A_1 and A_2 and the isotropy factor, $2C_{44}/(C_{11}-C_{12})$ were left unchanged, but $B_1=-B_2$. The rationale for the last condition stated is that the *sum* of the forces T_1 and T_2 on the first two surface layers will be zero before relaxa-

TABLE IV. Relaxations of atomic layers near a (100) surface in a modified Cu lattice.

Layer	Displacement[a]	Relative displacement[b]
1	3.813×10^{-8}	+0.16821
2	−0.16821	−0.00156
3	−0.16977	+0.00002
4	−0.16979	+0.0
5	−0.16979	

[a] Positive displacement are toward the surface.

[b] Positive signs denote relative expansion, negative signs denote relative contraction.

tion takes place [see Eq. (25)]. The resulting force constants given in Table I indicate that the nearest-neighbor radial force constant A_1 is still 60 times as strong as A_2, just as in the bulk lattice, so that the interactions between nearest-neighboring layers are still dominant over those for the next-nearest-neighboring layers. One would expect the displacements to fall off fairly rapidly in this situation and the results of the displacement calculations, given in Table IV indicate that this is the case. At a "depth" of about three layers from the surface, the "uniform" relaxation has become constant and there is almost no relative displacement.

The set of modified force constants is not suitable for calculating displacements near the (110) surface, since both first *and* second layer interactions are strongly repulsive for that orientation. In the case of the (111) surface T_2 is identically zero and, as in the case of the (110) surface in a bcc material, only a uniform relaxation should occur. Numerical results were not obtained for this case.

IV DISCUSSION

As emphasized earlier, the most important aspect of the present work is the development of a general workable formalism for calculating atomic displacements in the vicinity of surfaces on semi-infinite slabs of monatomic materials in such a way that all of the atoms of the lattice are allowed to relax simultaneously. The interatomic potentials employed in the calculations described in Sec. III were not true surface potentials but pairwise interactions derived from force constants suitable for calculations in bulk lattices. Nevertheless, there are certain general characteristics of the lattice symmetry and surface orientation which appear in the numerical results of these calculations.

It is significant, first of all, that while the formalism developed in Sec. II is capable of predicting tangential components of displacement, the form of the $(V^{-\vec{q}})^{-1}$ matrix for each of the high-symmetry surface orientations considered makes possible only normal components of relaxation, regardless of the atomic interaction used, as predicted by other authors.[5,8] In the case of the (110) surface in α-iron and the (111) surface in Cu, where there are only surface-induced forces on the surface layer itself (assuming only first- and second-neighbor atomic interactions) there are no *relative* displacements between adjacent layers near the surface, but only a uniform "continuum" relaxation of the lattice. The same effect is apparent in the results shown in Table II for relaxations near a (100) surface in Cu. In this case, the nearest-neighbor force constants for Cu are so much stronger than those for the second neighbor that the relative displacements of the atomic layers are very small and die out rapidly with increasing distance from the surface.

In the case of the (100) surface for α-iron, the first- and second-neighbor force constants are much closer in value and the forces induced on the first and second planes of the surface are nearly equal and opposite. As a result the "uniform" contribution to the atomic relaxations is relatively small. This is reasonable in light of the work done by Gazis and Wallis[9] which shows that the uniform relaxation is proportional to the sum of the surface-induced forces on the atomic planes at the surface. The relative displacements, however, are reasonably large for the first three layers, dying out rapidly, as before, with increasing distance from the surface. An interesting characteristic of the relative displacements is the alternating sign of the displacement, indicating that certain pairs of atomic planes are closer together after relaxation than they were before. The last case remaining to be discussed is that of the (111) surface for a bcc lattice, which is unique in that there are surface-induced forces on the first three layers of the surface. These forces are much smaller in magnitude than the forces on the first two layers of the (110) surface in α-iron, possibly because of the relative openness of the bcc lattice in the ⟨111⟩ directions. Consequently the total displacements of the first 20 layers near the surface are small. The relative displacements do not decrease in magnitude with distance from the surface as rapidly as for other surface orientations, a behavior very reminiscent of atomic relaxations about a vacancy in bcc materials for atoms along the ⟨111⟩ directions in the lattice.

The "uniform" displacement encountered in the present work is a direct consequence of using a short-range bulk potential to describe surface conditions and partially due to neglecting anharmonic contributions to the lattice relaxation. The bulk potentials, in general, impose an internal compression or expansion of the bulk lattice, such that the mathematical model of surface formation resembles clipping a spring which is originally under tension or compression. The ensuing relaxation involves a uniform increase in the separation between coils. If there are a large number of coils closely spaced, the increase in the "inter-coil" separation is small, but the over-all displacement of first few coils near the "cut" may be large. Such a " uniform" displacement would not be encountered, *per se*, if a long-range potential, such as a Morse potential, were used, especially if a finite number of layers were relaxed, since there would be no way of distinguishing between the "uniform" contribution and the remainder of the relative displacement. In the present case, it would probably be unwise to attach much real significance to the "uniform" component of the relaxation.

It is apparent, especially in the case of Cu, that bulk potentials (or force constants) cannot accurately describe the interactions of atoms near the surfaces of a crystal, yet these potentials must still be used to determine the relaxations of atoms below the first few surface layers. The "exact" lattice statics approach is inadequate to handle surface calculations in which interatomic potentials vary as a function of depth within the crystal, and for which anharmonic effects are very likely important. However, the "modified" lattice-statics approach,[13] in which surface-induced forces on the first few atomic layers of a surface can be treated exactly and the remainder of the crystal relaxed harmonically, can be used to give more reliable numerical values of atomic relaxations, once suitable interatomic potentials for surfaces are available. Work is currently progressing on such modified lattice statics calculations.

As mentioned in Sec. I, the short-range potentials used in this paper differ considerably from the potentials used by others; the Morse potential was used in Refs. 3, 4, and 6 and the Mie potential in Ref. 5. Both of these types of potential are long range in nature and the Morse potential, in particular, is known to give large displacements for atoms in the vicinity of point defects in bulk lattices, compared to those obtained from short-range potentials. However, Jackson[6] has drawn some general conclusions concerning the relative sizes of displacements at high-symmetry surfaces for bcc and fcc lattices, with which some comparison may be made. Jackson found that for bcc lattices the greatest relaxation occurred for the (111) surface and the least for (110). For the fcc lattice the order was (110) > (100) > (111). In the present α-iron results, the displacement of the (100) surface layer is greater than that for the (111) layer, which is exactly opposite to Jackson's conclusion. This result is not surprising, since the tangential force constants B_1 and B_2 obtained from the Morse potential differ greatly in magnitude from each other, while those for the Johnson potential are nearly equal. The calculations performed for fcc metals are insufficient to allow a similar comparison for that case.

Considering the deficiencies in the potentials used, the directions and magnitudes of both the total displacements and relative displacements seem reasonable. More reliable results must await the development of surface potentials which realistically reflect the redistribution of electrons in the vicinity of the surface.

V. SUMMARY

The lattice-statics formalism employed previously in determining atomic relaxations near point defects and dislocations in bulk lattices[10-12] has been applied to determine atomic relaxations in the vicinity of surfaces in bcc and fcc materials in the form of semi-infinite slabs. The formalism developed has been used to calculate the displacements of atomic layers in the vicinity of (100), (110), and (111) surfaces in α-iron and Cu.

The lattice-statics approach allows all of the atoms in the model lattice to relax simultaneously in the presence of the surface, but is accurate, strictly speaking, only within the limitations of the harmonic approximation. However, anharmonic effects can be accounted for by a simple modification of the present formalism, as outlined in Ref. 13 for point-defect problems. In addition, the potentials used in the present calculation are actually intended for calculations in bulk crystals, since reliable surface potentials for metals do not appear to be available at present. The numerical results obtained are only intended to demonstrate the application of the lattice statics approach to practical surface problems and are not to be compared to experimental or other theoretical results. However, the atomic relaxations obtained seem reasonable and appear to possess some of the general characteristics of surface displacements noted by others.[3-6,9]

The lattice statics formalism developed for application to surface problems is quite general for monatomic lattices and can be used, with minor modifications, to investigate the properties of surfaces having lower symmetry than those considered here and to determine the nature of interactions between surfaces and point defects within the crystal.

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[1] S. Maiya and J. Blakely, J. Appl. Phys. 38, 698 (1967).

[2] R. L. Schwebel, J. Appl. Phys. 38, 3154 (1967).

[3] P. Wynblatt and N. A. Gjostein, Surf. Sci. 12, 109 (1968).

[4] P. Wynblatt and N. A. Gjostein, Surf. Sci. 22, 125 (1970).

[5] F. Bonneton and M. Drechsler, Surf. Sci. 22, 426 (1970).

[6] D. P. Jackson, Can. J. Phys. 49, 2093 (1971).

[7] T. E. Feuchtwang, Phys. Rev. 155, 715 (1967).

[8] A. Corciovei, M. Croitoru, and D. Grecu, Surf. Sci. 21, 109 (1970).

[9] D. C. Gazis and R. F. Wallis, Surf. Sci. 3, 19 (1964).

[10] J. R. Hardy and J. W. Flocken, Phys. Rev. 175, 914 (1968).

[11] J. W. Flocken, Phys. Rev. B 4, 1187 (1971).

[12] L. L. Boyer and J. R. Hardy, Philos. Mag. 24, 647 (1971).

[13] J. W. Flocken, Phys. Rev. B 6, 1176 (1972).

[14] R. A. Johnson, Phys. Rev. 134, A1329 (1964).

[15] J. W. Flocken and J. R. Hardy, Phys. Rev. 177, 1054 (1969).