Oscillatory relaxation of a surface with a large penetration depth

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A theory is derived for the relaxation of a surface in a conducting crystal. This relaxation is the sum of an ordinary, exponentially decaying, relaxation and an oscillatory relaxation which falls off slowly with distance into the interior, in accordance with a power law. The oscillatory component is ultimately due to Friedel oscillations of the electron density, a consequence of the fact that there is a surface. These oscillations are transmitted to the lattice by electron-phonon coupling.

1. INTRODUCTION

Although research on the deformation of finite-size particles dates back quite far, this question can by no means be regarded as finally resolved. On the one hand, we know that the surface layers of a crystal are separated from each other by a distance different from that in the interior. It is generally assumed that this deformation of the lattice (surface relaxation) decays rapidly with distance from the surface. On the other hand, there is the widespread view that finite-size crystals experience a uniform compression because of the Laplace pressure. This point of view is advanced in Ref. 1, among other places. The error of that approach was proved in Refs. 2 and 3, and we will not discuss that question here. We simply assert that the deformation of the lattice of a small particle, if it is not charged, also reduces to a surface relaxation. Only in the case of charged particles does a uniform bulk deformation arise. As was shown in Ref. 4, despite the general belief that the charging of particles always causes them to expand, there can be situations in which the particles may also be compressed.

In this paper we offer a detailed analysis of the surface relaxation of conducting particles. We show that in addition to the ordinary relaxation, which decays exponentially with distance into the interior, there is also an oscillatory relaxation, which decays as a power law with distance into the interior. The physical origin of this oscillatory relaxation is the circumstance that the truncation of the crystal lattice at the surface of the crystal gives rise to Friedel oscillations in the electron density. The electron-phonon interaction induces analogous oscillations in the distance between atomic layers. These two relaxation components coexist and affect each other.

An oscillatory relaxation has been seen experimentally in many metals (Al, Fe, V, etc.) and at various crystallographic faces (Refs. 5–7, for example). In the theoretical interpretation of this relaxation in Refs. 8–11, however, the possibility that the oscillations are of Friedel origin was not considered (numerical calculations were carried out in those studies on the basis of models using the concept of a self-consistent pseudopotential, but the results were interpreted by appealing to qualitative arguments which apply more properly to insulators than to metals; this approach led to the assumption that the relaxation amplitude falls off exponentially).

2. MODEL OF SURFACE RELAXATION

In the absence of conduction electrons, the relaxation of a surface is caused exclusively by ion-ion interactions, and (as we will show below) this relaxation occurs if we go beyond the nearest-neighbor approximation in calculating the elastic energy. In principle, for insulators having a high compressibility the relaxation caused by this mechanism could penetrate to a significant depth. Since this effect occurs near the boundary of a region of absolute stability of the lattice, however, it is not clear whether the resulting structure could be stable. It may be that this effect could be observed in metastable states of insulating crystals.

It would thus be natural to expect that the surface relaxation in a conductor would be the sum of the oscillatory Friedel relaxation and a component which falls off more rapidly. The latter component, however, should also depend strongly on the electron subsystem. In metals, the elastic interactions between ions arise because their charges are screened by electrons, so one cannot simply introduce elastic constants in them without electrons. In degenerate semiconductors, the situation is different. The conduction electrons, along with ionized donors, simply renormalize the elastic interactions in the crystal. The effect of impurity atoms on the deformation of the lattice of a semiconductor should obviously be proportional to the concentration ν of these atoms (we are assuming that the atoms do not form clusters and that the number of conduction electrons is thus equal to the number of donors). With regard to conduction electrons we note that it follows from the calculation below that the effect of these electrons on the relaxation is proportional to a lower power of ν at values $\nu \sim 10^{20}$–10^{21} cm^{-3}. We will accordingly ignore the effect of impurity atoms.

The nature of Friedel oscillations may be influenced substantially by the electron-electron interaction, which results in screening of the charge which forms at the surface of the crystal (for example, if a crystal can be thought of as a potential well of infinite depth, the electron wave functions would vanish at the surface of the crystal, so the charge of the positive ions would not be canceled). To simplify the calculations below we will assume that the thickness of the film is smaller than the screening radius. At a thickness of 100 Å this condition holds for heavily doped narrow-gap semiconductors and for several semimetals.

The calculations below show that it is indeed possible to separate the surface relaxation into slowly and rapidly decaying components. For semiconductors we find the relaxation amplitude as a function of the concentration of conduction electrons. In certain cases the relaxation is determined essentially entirely by the conduction electrons.

In the calculation method which we use below, problems associated with diagonalizing the Hamiltonian of the

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zeroth approximation in the electron-phonon coupling in a crystal of finite dimensions are circumvented by using a site representation and by calculating the level density directly.

For definiteness we consider a crystal with a simple cubic lattice, bounded by two (001) plane surfaces. We assume that no restructuring of the surface occurs. The problem of determining the crystal structure of the sample is thus reduced to the one-dimensional problem of the equilibrium interplanar distances a_n ($n = 1,2,...,L-1$; L is the number of atomic layers in the sample). The values of a_n can be found by minimizing the total energy of the crystal, written as a function of these variables, with respect to them. The calculations are carried out for a simple model with the Hamiltonian

$$H=H_{(e)}+H_{(a)}, \tag{1}$$

$$H_{(e)}=\sum_{n,\mathrm{g}} B(a_n)(c_{n\mathrm{g}}^{+}c_{n+1,\mathrm{g}}+c_{n+1,\mathrm{g}}^{+}c_{n\mathrm{g}})$$
$$+B(a)\sum_{n,\mathrm{g},\delta} c_{n\mathrm{g}}^{+}c_{n,\mathrm{g}+\delta}+\sum_{n,\mathrm{g}} U(n)\,c_{n\mathrm{g}}^{+}c_{n\mathrm{g}}, \tag{2}$$

$$H_{(a)}=L_s^2\sum_{n=1}^{L-1}\varphi_1(a_n)+L_s^2\sum_{n=1}^{L-2}\varphi_2(a_n+a_{n+1}). \tag{3}$$

The operators c_{ng}^{+} and c_{ng} in (2) are electron operators in the site representation; the index n corresponds to a count of the lattice sites along the normal to the surface; g runs along the surface; and δ numbers the nearest neighbors along the surface. In accordance with the assumptions listed above regarding the nature of the deformation of the lattice, we take account of the dependence of the Bloch integral B for transitions along the normal to the surface on the distance between the corresponding atomic planes, a_n. The Hamiltonian $H_{(a)}$ given by (3) describes elastic interactions without consideration of electrons. It incorporates only the uniaxial nature of the deformation; the energy described by (3) thus depends on only the interplanar distances a_n. In order to obtain a surface relaxation we must go beyond the approximation which incorporates the interactions only between nearest neighbors. We restrict the present analysis to the interactions among next-nearest neighbors [the second term in (3)]. Finally, L_s^2 is the number of sites in each atomic layer.

Assuming that the deviations α_n of the lattice constant from its bulk value a are small $a(\alpha_n \equiv a_n - a, |\alpha_n| \ll a)$, we write the total energy as an expansion in α_n (we are leaving these quantities arbitrary). Determining the value of a from the condition that there be no terms linear in α_n in the interior of a sufficiently thick sample, we find the following expression from (1)–(3):

$$\mathscr{E}=\mathscr{E}_0-L_s^2\sum_{n=1}^{L-1}f_n\alpha_n+{}^1/_2L_s^2\sum_{m,n=1}^{L-1}g_{nm}\alpha_m\alpha_n, \tag{4}$$

where

$$f_n=f_n^{(e)}+f^{(a)}(\delta_{n1}+\delta_{n,L-1}), \tag{5}$$

$$\mathscr{E}_0=\mathscr{E}_0^{(e)}+(L-1)L_s^2\varphi_1(a)+(L-2)L_s^2\varphi_2(2a), \tag{6}$$

and g_{mn} has the nonvanishing elements

$$g_{12}=g_{23}=\ldots=g_{L-2,L-1}=Q,\quad g_{22}=g_{33}=\ldots=g_{L-2,L-2}=P+2Q,$$
$$g_{11}=g_{L-1,L-1}=P+Q,\quad P\equiv\varphi_1''(a),\quad Q\equiv\varphi_2''(2a).$$

The remaining terms in (4) which are linear in α_n result from the effect of the crystal surface. According to (5), f_n has additive components from both the atomic and electron subsystems. For the atomic subsystem we have $f^{(a)} = \varphi_2'(2a)$ and $\varphi_2'(2a) = -\varphi_1'(a)/2$; the coefficients $f_n^{(e)}$ will be calculated below (Sec. 3).

The particular form of Eqs. (4)–(6) presupposes that the dependence of the electron density on the displacements is dealt with in the linear approximation, as usual. The effect is to ignore the influence of electrons on the elastic constants of the crystal. We will derive an expression for the electron energy as a function of the quantities α_n, taking the quantum size effect into account in the limit of a large but finite crystal thickness ($L \gg 1$). For the particular type of lattice and the particular type of lattice boundary which we have selected, the energy of a one-electron state with a wave vector $\mathbf{k}_\parallel = (k_x, k_y)$ along the surface of the crystal is $E_j(\mathbf{k}_\parallel) = E_\parallel(\mathbf{k}_\parallel) + \varepsilon_j$, and $E_\parallel(\mathbf{k}_\parallel) = 2B(\cos k_x + \cos k_y)$, and ε_j is found from the equations for the wave function $\Psi_{ng} = \psi_n \exp(i\mathbf{k}_\parallel g)$ in the site representation:

$$\begin{pmatrix} \varepsilon-U_1 & -B_1 & 0 & \ldots & \ldots & 0 \\ -B_1 & \varepsilon-U_2 & -B_2 & \ldots & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & \ldots & \ldots & -B_{L-1} & \ldots & \varepsilon-U_L \end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\\ \vdots\\ \psi_L\end{pmatrix}=0. \tag{7}$$

Here $B_n \equiv B(a_n)$, $B \equiv B(a)$. The spectral values ε_j are the roots of the determinant of system (7); we denote this determinant by D_{1L}, explicitly stating the interval of lattice-site indices which figure in Eqs. (7). To determine D_{1L} we write (7) as a second-order difference equation with boundary conditions

$$B_{n-1}\psi_{n-1}+B_n\psi_{n+1}=(\varepsilon-U_n)\psi_n,$$
$$\psi_{l-1}=\psi_{m+1}=0\quad (n=l,\,l+1,\ldots,m). \tag{8}$$

In accordance with (7) we should set $l = 1$ and $m = L$. The general solution of (8) is known[12] to depend on two arbitrary constants, which can be found from one of the boundary conditions (e.g., $\psi_0 = 0$) and from the normalization condition. The second boundary condition, $\psi_{L+1} = 0$, then becomes an equation for ε, whose solution determines the spectral values ε_j. However, since the normalization factor depends on ε, that equation cannot be an algebraic equation of degree L in ε; i.e., in general, its solution would contain extraneous roots. Using (7) and (8), one can easily show that the appearance of such roots can be avoided by adopting a normalization condition of the form $\psi_1 = 1$. In this case,

ψ_n is a polynomial of degree $n-1$ in ε. In particular, ψ_{L+1} is a polynomial of degree L in ε and thus agrees to within a numerical factor with the determinant which we are seeking, $D_{1L}(\varepsilon)$.

It follows from the general properties of determinants that D_{1L} is a multilinear function of $(B_n/B)^2$. In this case we have $D_{1L} = D_{1n}D_{n+1,L} - D_{1,n-1}D_{n+2,L}(B_n/B)^2$, where the determinants on the right side do not depend on B_n (although they do depend on the other B_m with $m \neq n$). In the approximation linear in α_n we would have $(B_n/B)^2 = 1 + \lambda_n$, where $\lambda_n = \gamma\alpha_n$, and $\gamma = 2B'(a)/B(a)$. Making use of the small quantities λ_n, we then find

$$D_{1L} \approx D_{1L}{}^0 + \sum_{n=1}^{L} \varkappa_n \lambda_n, \tag{9}$$

where $\varkappa_n = -D^0_{1,n-1}D^0_{n+2,L}$, and D^0_{nm} is the value of D_{nm} in the case $\lambda_n \equiv 0$.

3. LEVEL DENSITY IN A DEFORMED CRYSTAL

The number of electron states and the sum of their energies for a Fermi distribution with a Fermi energy E_F are calculated from the expressions

$$\begin{gathered}
N(E_F) = \sum (L_s/2\pi)^2 \int d^2k_{\|}\theta[E_F - E_j(\mathbf{k}_{\|})] = \sum_j N_{\|}(E_F - \varepsilon_j), \\
\mathscr{E}^{(e)}(E_F) = \sum_j (L_s/2\pi)^2 \int d^2k_{\|} E_j(\mathbf{k}_{\|})\theta[E_F - E_j(\mathbf{k}_{\|})] \\
= \sum_j [\mathscr{E}_{\|}^{(e)}(E_F - \varepsilon_j) + \varepsilon_j N_{\|}(E_F - \varepsilon_j)],
\end{gathered} \tag{10}$$

where

$$N_{\|}(E) \equiv (L_s/2\pi)^2 \int d^2k_{\|}\theta[E - E_{\|}(\mathbf{k}_{\|})],$$

$$\mathscr{E}^{(e)}(E) \equiv (L_s/2\pi)^2 \int d^2k_{\|} E_{\|}(\mathbf{k}_{\|})\theta[E - E_{\|}(\mathbf{k}_{\|})],$$

and $\theta(E)$ is the unit step function (or Heaviside function). We can find an estimate of the sums (10) in the limit $L \gg 1$ by working from an equivalent expression for these sums in the form of contour integrals in a complex plane. For example, we have the standard expression

$$N(E_F) = (1/2\pi i)\oint_{C_E} dE\, N_{\|}(E_F - E)\tilde{\omega}(E), \tag{11}$$

where

$$\tilde{\omega}(E) = \sum_j (E - \varepsilon_j)^{-1} = (d/dE)\ln D_{1L}(E)$$

is the trace of the Green's function for Eq. (7). In (11) it is convenient to transform to the new integration variable k: $\varepsilon = 2B\cos k \equiv \varepsilon(k)$. We then have

$$N(E_F) = (1/2\pi i)\oint_C dk\, N_{\|}[E_F - \varepsilon(k)]\omega(k), \tag{12}$$

where

$$\omega(k) \equiv (d/dk)\ln D_{1L}(\varepsilon(k)),$$

and C is a contour in the k plane which corresponds to a summation over states of a Fermi distribution with a Fermi energy E_F.

Specific calculations will be carried out for the case in which the conduction band is only sparsely populated, and the effective-mass approximation can be used. In this case we have $E_j(\mathbf{k}) = E(0) + |B|(\mathbf{k}_{\|}^2 + k_j^2)$, where k_j is the quasimomentum component directed perpendicular to the surface. It is convenient to replace E_F by the Fermi momentum k_F: $E_F = E(0) + |B|k_F^2$. We then find, in place of (10),

$$\begin{gathered}
N(k_F) = \frac{L_s{}^2}{4\pi}\sum_{k_j}(k_F{}^2 - k_j{}^2)\theta(k_F{}^2 - k_j{}^2), \\
\mathscr{E}^{(e)}(k_F) = \frac{L_s{}^2}{4\pi}\sum_{k_j}(k_F{}^2 - k_j{}^2) \\
\cdot\left[E(0) + \frac{|B|(k_F{}^2 + k_j{}^2)}{2}\right]\theta(k_F{}^2 - k_j{}^2),
\end{gathered} \tag{13}$$

where for the case $E_F > E(0)$, for example, the summation incorporates all k_j such that the relations $0 < k_j < k_F$ hold and all values $k_j = i\varkappa_j$ which correspond to the presence of surface subbands below the bottom of the interior band (they may also arise from deformation of the crystal). Correspondingly, in place of (12) we will have

$$N(k_F) = \frac{L_s^2}{8\pi^2 i}\oint_C dk\,(k_F{}^2 - k^2)\,\omega(k), \tag{14}$$

where the contour C is shown for the case $E_F > E(0)$ in Fig. 1(a), where the points are the spectral values k_j, and the value $\bar{k}$ is defined in such a way that the contour C includes all values k_j which correspond to a Fermi distribution with a Fermi momentum k_F. In this case, $\bar{k}$ and k_F obviously lie in the same gap between spectral values k_j, and there is naturally some arbitrariness in the choice of $\bar{k}$ ($\bar{k} = k_F + \eta$, where $|\eta|$ is sufficiently small). Expression (14) simplifies substantially when we make use of the fact that the integrand in (13) is even in k in the case $\operatorname{Im} k = 0$:

$$2N(k_F) = \frac{L_s^2}{8\pi^2 i}\oint_{\bar{C}} dk\,(k_F{}^2 - k^2)\,\omega(k). \tag{15}$$

The contour $\bar{C}$, shown in Fig. 1(b), is symmetric about the origin. The integral in (15) is a double sum over all values $k_j > 0$, so twice the value of $N(k_F)$ appears on the left. Since the integrand is a real function of a complex argument {i.e., $[\omega(k)]^* = \omega(k^*)$, for example}, we find from (15)

$$N(k_F) = \frac{L_s^2}{4\pi}\operatorname{Re}\frac{1}{2\pi i}\int_{\bar{C}^+} dk\,(k_F{}^2 - k^2)\,\omega(k), \tag{16}$$

where $\bar{C}^+$ is the part of contour $\bar{C}$ which is in the upper half-plane.

In calculating $\omega(k)$ below we restrict the analysis to the case in which we can ignore the external field U_n in (7) and (8); such a field might be caused by the presence of the surface. Using Laplace transforms, we then find from (8)

$$D_{lm}{}^0(k) = \sin[(m - l + 2)k]/\sin k. \tag{17}$$

Using (9), we find the following expression for $\omega(k) \equiv (\ln D_{1L}(k))'$:

$$\omega(k) = \omega^0(k) + \sum_{n=1}^{L-1}\lambda_n\mu_n{}'(k), \tag{18}$$

where

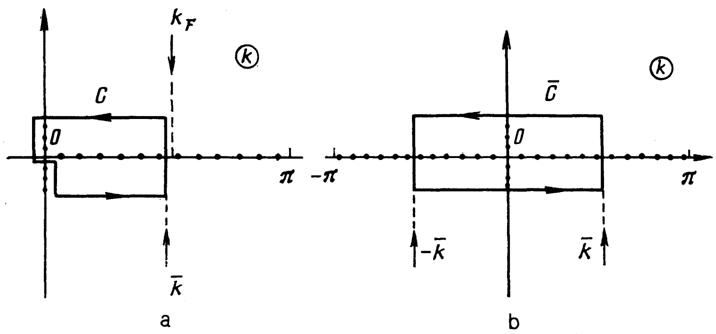

FIG. 1.

$$\omega^0(k)=(L+1)\operatorname{ctg}[k(L+1)]-\operatorname{ctg} k, \tag{19}$$

$$\mu_n(k)=\frac{\cos kL-\cos k(L-2n)}{2\sin k\sin k(L+1)}.$$

The asymptotic estimate of $N(k_F)$ at $L\gg 1$ which we are seeking is found from (16) with the help of (17)–(19):

$$N(k_F)\sim-\frac{L_s^2}{8\pi}k_F^2+\frac{2}{3}\frac{L_s^2}{4\pi}\frac{L+1}{\pi}k_F^3$$

$$+\frac{L_s^2}{4\pi^2}k_F\sum_{n=1}^{L-1}\lambda_n\left[1-\frac{\sin(2k_F\bar{n})}{2k_F\bar{n}}\right] \tag{20}$$

Here and below, the quantity $\bar{n}=\bar{n}(n)$ is defined in such a way that we have $\bar{n}\sim n$ at $1\lesssim n\lesssim L/2$ and $\bar{n}\sim L-n$ at $L/2\leqslant n\leqslant L$. The details of the calculations of (17)–(20) are given in the Appendix. Working from (13) in a similar way, we find the asymptotic behavior of the electron energy $\mathscr{E}^{(e)}$:

$$\mathscr{E}^{(e)}\sim\left[E(0)+\frac{|B|k_F^2}{2}\right]N(k_F)+\frac{|B|}{15}\frac{L_s^2}{4\pi}\frac{L+1}{\pi}k_F^5$$

$$-\frac{L_s^2}{24\pi^2}|B|k_F^3\sum_{n=1}^{L-1}\frac{\lambda_n}{(k_F\bar{n})^2}\Big\{(k_F\bar{n})^2 \tag{21}$$

$$+\frac{3}{2}k_F\bar{n}(1-(k_F\bar{n})^{-2})\sin(2k_F\bar{n})$$

$$+3\cos(2k_F\bar{n})\Big\}.$$

Eliminating k_F from (21) with the help of (12), and comparing the resulting expression with (4)–(6), we find a relation for the quantities involved there:

$$\mathscr{E}_0^{(e)}\approx\left[E(0)+\frac{3}{5}|B|k_0^2\right]L_s^2L\nu+|B|\frac{L_s^2}{8\pi}k_0^4,$$

$$f_n^{(e)}\approx-\frac{B'}{2\pi^2}k_0\frac{1}{\bar{n}^2}\left[\cos 2k_0\bar{n}-\frac{\sin 2k_0\bar{n}}{2k_0\bar{n}}\right]. \tag{22}$$

Here $\nu\equiv NL_s^{-2}/(L+1)$, and $k_0\equiv(3\pi^2\nu)^{1/3}$ is the value of the Fermi momentum for a bulk sample ($L\to\infty$).

4. LATTICE DEFORMATION

Minimizing the energy functional (4) with respect to α_n, we find equations for these variables. If we single out the translationally invariant bulk part g^0_{mn} in the matrix g_{mn}, we can rewrite these equations as

$$\sum_{m=1}^{L-1}g^0_{|n-m|}\alpha_m=(\delta_{n1}+\delta_{n,L-1})f^{(a)}+f_n^{(e)}+Q(\alpha_0+\alpha_1)\delta_{n1}$$

$$+Q(\alpha_{L-1}+\alpha_L)\delta_{n,L-1}, \tag{23}$$

where $g^0_{|n-m|}\equiv g^0_{nm}$ has two nonvanishing elements: $g^0_0=P+2Q$, $g^0_1=Q$. A solution of (23) can be written in the form

$$\alpha_n=\sum_{m=1}^{L-1}G_{nm}^0f_m^{(e)}+\frac{G_{n1}^0+G^0_{n,L-1}}{1-Q(G_{01}^0+G_{11}^0+G^0_{0,L-1}+G^0_{1,L-1})}$$

$$\cdot\left[f^{(a)}+Q\sum_{m=1}^{L-1}(G_{0m}^0+G_{1m}^0)f_m^{(e)}\right], \tag{24}$$

where G^0_{nm} is the Green's function (the inverse matrix) for the matrix g^0_{nm}, given by

$$G_{nm}^0=\theta^{-|n-m|}[Q(\theta^{-1}-\theta)]^{-1}. \tag{25}$$

Here

$$\theta=-(1+P/2Q)\pm[(1+P/2Q)^2-1]^{1/2}, \tag{26}$$

and the sign should be chosen to satisfy $|\theta|>1$. Expression (24) is the basic result of this study.

From (24) we can find an approximate expression for α_n by noting that the Green's function (25) falls off exponentially with increasing $|n-m|$, while the oscillation amplitude $f_n^{(e)}$ depends on n in accordance with a power law, and the frequency is relatively low. We then have

$$\sum_{m=1}^{L-1}G_{nm}^0f_m^{(e)}\approx f_n^{(e)}\Gamma_n,\quad \sum_{m=1}^{L-1}(G_{0m}^0+G_{1m}^0)f_m^{(e)}\approx f_1^{(e)}(\Gamma_0+\Gamma_1),$$

$$\Gamma_n\equiv\sum_{m=1}^{L-1}G_{nm}^0,$$

in (24), and as a result, we find

$$\alpha_n\approx\Gamma_nf_n^{(e)}+R_n[f^{(a)}/Q+(\Gamma_0+\Gamma_1)f_1^{(e)}], \tag{27}$$

where

$$R_n\equiv-(\theta^{n-L/2}+\theta^{-n+L/2})(\theta^{1/2}+\theta^{-1/2})(\theta^{(L-1)/2}+\theta^{(-L+1)/2})^{-1},$$

$$\Gamma_n=(P+4Q)^{-1}[1+(1+\theta^{1-L})R_n].$$

The behavior of the functions Γ_n and R_n depends on the parameter θ, which, according to (26), depends on the ratio of the stiffness coefficients for the interactions of neighbors separated by various amounts. It is clear from physical considerations that if there is no interaction φ_2 between next-nearest neighbors we would have $R_n\equiv 0$ for all n from 1 to $L-1$. This assertion can also be verified directly on the basis of the expression given above for R_n. Specifically, when we let $Q\to 0$ we have $|\theta|\sim|P/Q|$, according to (26); in this case we have $|R_n|\leqslant R_1|\sim|\theta|^{-1}$, $|\theta|\to\infty$.

We can distinguish three cases:

I. $P \geqslant 0$, $Q > 0$. In this case we have $\theta < 0 (\theta = -e^{\mu})$ and

$$R_n = \frac{(-1)^{n+1}}{2} \cdot \begin{cases} \dfrac{\operatorname{ch}[\mu(-n+L/2)]}{\operatorname{sh}(\mu/2)\operatorname{sh}[\mu(L-1)/2]}, \\ \text{for even } L; \\ \dfrac{\operatorname{sh}[\mu(-n+L/2)]}{\operatorname{sh}(\mu/2)\operatorname{sh}[\mu(L-1)/2]}, \\ \text{for odd } L. \end{cases} \tag{28}$$

II. $Q < Q$, $P \geqslant 4|Q|$. In this case we have $\theta > 0$ $(\theta = e^{*})$ and

$$R_n = -\frac{\operatorname{ch}\varkappa(-n+L/2)}{2\operatorname{ch}(\varkappa/2)\operatorname{ch}[\varkappa(L-1)/2]}. \tag{29}$$

III. $Q < 0$, $2|Q|[1 + \cos \pi/(L-1)] < P < 4|Q|$. In this case we have $\operatorname{Im}\theta \neq 0$, $|\theta| = 1$, $\theta = \exp(ik)$ and

$$R_n = -\frac{\cos[k(-n+L/2)]}{2\cos(k/2)\cos[k(L-1)/2]}. \tag{30}$$

The expressions in (28)–(30) are given for those values of the parameters P and Q in which the equilibrium state of the system is stable against small displacements of plane layers as a whole normal to the surface. The stability condition reduces to the condition

$$\xi_n = P + 2Q\{1 + \cos[\pi n/(L-1)]\} > 0,$$

i.e., the condition that the eigenvalues ξ of the matrix g_{mn} must be positive.

From (20) and (27) we find the chemical potential of the electrons as a function of the thickness of the sample:

$$\frac{E - E_F^0}{E_F^0} \sim \frac{k_0^2}{6\pi\nu L}\left[\left(1 - \frac{4k_0}{3\pi}\right) + \frac{\gamma^2|B|k_0}{6\pi^2(P+4Q)} - \frac{4\gamma f^{(a)}k_0}{3\pi(P+2Q)}\right]. \tag{31}$$

This estimate was derived under the assumptions $k_0 \lesssim 1$, $k_0 L \gg 1$, under the assumption $|\theta| \gtrsim 1$ in (26), and in the same approximations as were used in calculating expression (27).

5. DISCUSSION OF RESULTS

Equations (27)–(31) describe both the lattice deformation and the shift of the Fermi energy caused by this deformation. Relation (27) consists of two terms. The first term, $\sim \Gamma_n$, describes the lattice deformation caused by the nonuniformity of the electron density in a finite-size crystal. The physical meaning of this term can be understood quite easily by looking at the Hamiltonian of the electron-phonon interaction in its standard form:

$$H_{(e,ph)} \sim \sum_q \alpha_q \rho_{-q},$$

where ρ_{-q} and α_q are the Fourier components of the electron density and the deformation. The surface makes the electron-density distribution nonuniform, with the result that the average Fourier components $\langle \rho_q \rangle$ with $q \neq 0$ become nonzero. Singling out a term $\sim \langle \rho_{-q} \rangle$ in $H_{(e,ph)}$ corresponds to adding to the phonon Hamiltonian a term $\sim \alpha_q \langle \rho_{-q} \rangle$ which is linear in the displacements α_q. This term is eliminated by an ordinary transformation involving a displacement of normal coordinates. As a result, their equilibrium positions are shifted by an amount $\sim \langle \rho_{-q} \rangle / \omega_q$, where ω_q is the phonon frequency.

It can be seen from (22) that the coefficients $f_n^{(e)}$ exhibit oscillations superposed on a power-law decay as a function of distance from the surface, i.e., behavior which is actually of the Friedel type. The same behavior is exhibited by the lattice deformation induced by Friedel oscillations in the electron density (27). The lattice deformation induced by conduction electrons when an electric field is applied to a crystal was studied in Ref. 13. This field is screened by electrons, whose density falls off with distance from the surface into the interior of the crystal in accordance with a law similar to that for Friedel oscillations. In Ref. 13, however, there was no deformation of this sort in the absence of an external field, demonstrating a substantial difference between the physical situations studied in Ref. 13 and in the present paper.

The second term ($\sim R_n$) in (27) results from the cutoff of elastic interactions between surface atoms and their missing neighbors. In the absence of conduction electrons, this term would give rise to relaxation only if the interaction between next-nearest neighbors were nonvanishing $Q \equiv \varphi_2''(2a) \neq 0$). In fact, as was shown above, in the limit $\varphi_2 \to 0$ the coefficients R_n in (27) tend toward zero like Q. The second term in (27) is thus proportional to the quantity $f^{(a)} = \varphi_2'(2a)$, which vanishes in the case $\varphi_2(r) = 0$.

The qualitative behavior of the elastic deformation in the absence of conduction electrons depends on the signs of the coefficients P and Q. If P and Q are positive, this deformation falls off exponentially with distance from the surface, changing sign from layer to layer [see (28)]. If P and Q instead differ in sign, the sign of the deformation is constant [see (29)]. The depth to which this deformation penetrates is normally proportional to the lattice constant. Exceptional regions are those near the stability boundaries of a crystal: $P = 0$ at $Q > 0$ and $P = 4|Q|$ at $Q < 0$. In the first of these cases, it is $(Q/P)^{1/2}$, and in the second it is $(P/2|Q| - 2)^{1/2}$. For crystals of finite thickness in the case $Q < 0$, there is also a small interval of values $P \lesssim 4|Q|$ in which the crystal is relatively stable with respect to uniaxial deformations of this type. In this region, as we see from (30), the lattice deformation oscillates but does not decay. It is not clear, however, whether crystals in which a uniaxial deformation penetrates to a large depth are stable against small deformations of other types. It may be that in this region of values of the elastic parameters some other crystal structure will be more stable.

The appearance of conduction electrons changes the magnitude of relaxation such as that under consideration here. The reason for this change is that the electrons renormalize the elastic interaction between atoms. To first order in the displacements of the atoms—the approximation which we have used here—there is no renormalization of the second derivatives of the potentials of the interatomic interaction, $P = \varphi_1''$ and $Q = \varphi_2''$. The first derivatives, φ_1' and φ_2', on the contrary, are renormalized. Accordingly, the relaxation amplitude determined by the factor R_n in brackets in (27) is thus also renormalized. At conduction-electron densities 10^{20}–10^{21} cm^{-3}, for which we have $k_0 \sim 1$, this renormalization can be extremely significant, since Γ_1 is proportional to $\nu^{1/3}$, according to (22). Electrons play a particularly prominent role in the limit $Q \to 0$. In principle, in the case $\varphi_2 = 0$ a surface relaxation would become possible as a result of conduction electrons alone. Physically, this happens because the electrons renormalize the interaction not only between nearest neighbors but also between more remote neighbors.

To find some numerical estimates, we take account of the following considerations. If we link the lowering of the bottom of the conduction band to the bulk deformation by means of the relation $\Delta E_c = C_1 \Delta V/V$, where $\Delta V/V$ is the relative change in the volume, then we find the condition $\gamma = 2C_1/(za|B|)$, where z is the coordination number of the lattice, for the electron-phonon coupling constant $\gamma = 2B'/B$. If we write the elastic energy of the crystal in the form[1] $(1/2)VC_2(\Delta V/V)^2$, we find the relation $P, Q \sim aC_2$ as estimates of the elastic constants. With $k_0 \lesssim 1$ and $|\theta| \gtrsim 1$ we find from (22)–(27) that the displacement of the outermost atomic layer is $\alpha_1 = \alpha_1{}^{(e)} + \alpha_1{}^{(a)}$, where

$$\alpha_1{}^{(a)} \sim 2k_0{}^3 C_1/[\pi^2 za(P+4Q)], \quad \alpha_1{}^{(a)} \sim \theta^{-1} f^{(a)}/Q.$$

Assigning C_1 and C_2 the characteristic values $C_1 \sim 10$ eV and $C_2 \sim 5 \cdot 10^{23}$ eV/cm^3, and assuming $k_0 \sim 1$, $z = 6$, and $a \sim$ Å, we find $\alpha_1{}^{(el)}/a \sim (1-5)\%$. It is difficult to offer a specific numerical estimate of the quantity $\alpha_1{}^{(a)}$.

The difficulty is that if we adopt the estimate $\theta \sim P/Q$ for $Q \ll P$ in accordance with (26) we find $\alpha_1{}^{(a)} \sim \varphi_2'(2a)/\varphi_1''(a)$, so this estimate depends strongly on the structure of the potentials φ_1 and φ_2. Clearly, however, the contribution of the ion component will vanish exponentially with distance from the surface, as we have already mentioned, so $\alpha_n{}^{(a)}$ would normally be exponentially small at $n = 2$–3.

According to (31), the chemical potential E_F of a sample of finite thickness differs from that of a bulk sample, E_F^0. The first term describes the increase in E_F for samples of finite size which is caused by size quantization; this term was found in Ref. 2. The physical reason for the increase in E_F is an increase in the kinetic energy of the electrons due to the bounded size of the region in which they are localized. The second and third terms result from the deformation of the crystal. Incorporating these terms renormalizes the proportionality factor in the relation $\Delta E_F/E_F^0 \sim L^{-1}$, as can be seen from (31). The presence of a Friedel surface relaxation makes this coefficient increase, while the sign of the atomic contribution is the same as that of the quantity $f^{(a)} = \varphi_2'(2a)$ and can, in general, be arbitrary. The nature of the dependence on the last terms indicates that the effect of these mechanisms on E_F is manifested primarily through a change in the size of the sample due to the deformation. It can be shown that a Friedel deformation leads to a relative increase in the dimensions of a sample, while the sign of the deformation due to elastic interactions will be the same as that of $f^{(a)}$. For the characteristic parameter values given above and for the value $|B| \sim 0.5$ eV, we find that the second term in (31) is 1–5% of the first. The specific estimate of the contribution of the last term depends strongly on the structure of the elastic-interaction potentials φ_1 and φ_2 in (3). The ratio of the last term to the second is $\sim \varphi_2'(2a)/B'(a)$.

The effect of a deformation on E_F was estimated in Ref. 2 by a variational method, based on the assumption of a uniform deformation. The analysis presented above, which allows for variations in the deformation of the crystal, refines the results of Ref. 2. In principle, the results derived above can be generalized in a qualitative way to the case of metal particles: It can be assumed that Friedel oscillations propagate away from each face of the crystal, so the picture of the deformations of a small particle is a superposition of the Friedel oscillations from the various faces.

APPENDIX

1. According to Sec. 1, the dependence of the determinant D_{lm}^0 on the energy ε agrees within a numerical constant with the dependence $\psi_{m+1}(\varepsilon)$, found from Eq. (8) with $B_n = B$ and $U_n = 0$. The general solution of this equation is $\psi_n = C_1\theta_1^n + C_2\theta_2^n$, where $\theta_{1,2}$ are the roots of the "characteristic" equation $B(\theta + \theta^{-1}) = \varepsilon$. Since we have $\theta_1\theta_2 = 1$, by setting $\theta = e^{ik}$ and making use of the boundary condition $\psi_{l-1} = 0$, we find $\psi_n = C(k)\sin[k(n-l+1)]$, $\varepsilon = 2B\cos k$. As a result we find $\psi_{m+1} = C(k)\sin[(m-l+2)k]$. Fixing $C(k)$ by means of the condition $\psi_l = 1$, we find relation (17) for $D_{lm}^0(k)$.

2. Equation (20) was derived by expanding the right side of (16) powers of L^{-1} $(L \gg 1)$. Let us examine this procedure, first for the case in which there is no lattice deformation; in this case we have $\lambda_n \equiv 0$ and $\omega(k) = \omega^0(k)$ in (18). Although each term in expression (19) for ω^0 has a pole at $k = 0$, there is no such singularity in $\omega^0(k)$. In other words, $k = 0$ is not a spectral value. Making use of this result, we rewrite (16) as

$$N(k_F) = -\frac{1}{2}\frac{L_s{}^2}{4\pi}k_F{}^2 + \frac{L_s{}^2}{4\pi}\operatorname{Re}\frac{1}{2\pi i}\int_{\bar{C}^+} dk\,(k_F{}^2 - k^2)\,\bar{\omega}^0(k), \tag{A1}$$

where $\bar{\omega}^0(k) \equiv (L+1)\operatorname{ctg}[(L+1)k]$ is the first term in (19). This term is conveniently written as the sum

$$\bar{\omega}^0(k) = -i\Omega^0(k) + \Delta\bar{\omega}^0(k), \quad -i\Omega(k) \equiv \bar{\omega}^0(k)\big|_{(L+1)\operatorname{Im} k\to\infty}.$$

In this case we have $\Omega(k) = L+1$ and $\Delta\bar{\omega}^0(k) = (L+1)\exp[ik(L+1)]/\sin[k(L+1)]$. Expression (A1) then becomes

$$N(k_F) = -\frac{1}{2}\frac{L_s{}^2}{4\pi}k_F{}^2 + \frac{L_s{}^2}{4\pi}\frac{L+1}{2\pi}\int_{-\bar{k}}^{\bar{k}} dk\,(k_F{}^2 - k^2) + \Delta N. \tag{A2}$$

The function $\Delta\bar{\omega}^0(k)$ falls off rapidly for $(L+1)$ Im $k \to \infty$, so in calculating ΔN it is convenient to deform the contour C^+ by displacing its horizontal part to infinity. We would then have

$$\Delta N = \frac{L_s{}^2}{4\pi}\operatorname{Re}\frac{1}{2\pi i}\left\{\int_{\bar{k}+i0}^{\bar{k}+i\infty} - \int_{-\bar{k}+i0}^{-\bar{k}+i\infty}\right\}(k_F{}^2 - k^2)\,\Delta\bar{\omega}^0(k)\,dk. \tag{A3}$$

To estimate (A3) we use the Laplace method, and we choose $\bar{k} = k_F$. We then find, for example

$$\int_{\bar{k}+i0}^{\bar{k}+i\infty} dk\,(k_F{}^2 - k^2)\,\Delta\bar{\omega}^0(k) \sim (k_F{}^2 - k^2)\Big|_{k=k_F}$$
$$\times \int_{k_F+i0}^{k_F+i\infty} dk\,\Delta\bar{\omega}^0(k) + (k_F{}^2 - k^2)'\Big|_{k=k_F}$$

$$\times \int_{k_F+i0}^{k_F+i\infty} dk\,(k-k_F)\,\Delta\overline{\omega}(k)+\ldots, \tag{A4}$$

from which we see that the leading term asymptotically vanishes, and an estimate of the succeeding terms reveals $\Delta N \sim O(L_s^2/L)$. Accordingly, if we ignore small terms of this order in (A4) we can assume $\Delta N = 0$ in (A2). The remaining terms in (A2) correspond to the first two terms in (20).

It would seem pertinent to explain the motivation for choosing the value $k = k_F$ in (A3)–(A4). This choice is decidedly arbitrary. Specifically, the quantity $N(k_F)$ would not change if we varied $\bar{k}$ over the interval between nearest spectral values of k. The total electron energy $\mathscr{E}^{(e)}(k_F)$ depends similarly on $\bar{k}$. If we eliminate k_F from these expressions, we find that the N dependence of $\mathscr{E}^{(e)}$ is in the form of a series in powers of L^{-1}. The coefficients of the series cannot depend on this arbitrariness in the choice of $\bar{k}$, since the accuracy of the estimate found when we truncate this series is also independent of the choice of $\bar{k}$. The choice can be made on the basis of considerations of convenience (as was done above). If we assume $\bar{k} \neq k_F$ in (A4), we find $(K_F^2 - k^2)|_{k=kF} \neq 0$, but this quantity is of order of magnitude $O(1/L\rangle$ since we have $|k_F - k| \sim 1/L$ in the gap between nearest points in the spectrum. Accordingly, the estimate $\Delta N \sim 0$ continues to hold, in accordance with the discussion above.

The asymptotic behavior for terms $\sim \lambda_n$ in (18) is found analogously. We should find the limits as L Im $k \to \infty$ of the functions μ_n in (19). The difference μ_n and its asymptotic expression will be functions which fall off exponentially as Im $k \to \infty$ with a decay rate $\sim L$. The asymptotic behavior of μ_n will generally take different forms for different values of n:

$$\mu_n(k) \sim [1-\exp(2ikn)]/[1-\exp(-2ik)] \equiv -iM_n(k) \tag{A5}$$

for $n \sim 1$ and $\mu_n(k) \sim [1-\exp(-2ik)]^{-1}$ for $n \sim L/2$. Although it would go beyond the accuracy of this treatment to incorporate the term $\sim \exp(2ikn)$ at $n \sim L/2$ in (A5), we are retaining it since we are treating (A5) as an interpolation for $1 \lesssim n \lesssim L/2$. At $L/2 \lesssim n \lesssim L$ we should bear in mind that M_n, along with μ_n, is symmetric about the middle of the sample. Expression (20) was derived in the effective-mass approximation [in which we have $|k| \ll 1$ in (A5)] and with allowance for spin degeneracy.

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1) For a plane we would have $C_2 = \mathscr{E}_J(1-\sigma_p)/1+\sigma_p)(1-2\sigma_p)$, where $\mathscr{E}_j$ is Young's modulus, and σ_p is the Poisson ratio.

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