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Lattice relaxation at a metal surface

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It is shown that all interatomic potentials of the classical type—Morse, Lennard-Jones, etc.,—yield, by their very nature, an expansion of the interlayer separation between the topmost surface layers. No such prediction can be made *a priori* for the oscillatory-type potentials. Using a simple procedure to compute the relaxations, we also show that Friedel's tight-binding model for transition metals yields contraction for the (100), (110), and (111) surfaces of a face-centered-cubic transition metal, a result in agreement with experiment.

I. INTRODUCTION

Over the last few years experimental data from low-energy electron diffraction (LEED) experiments on clean metal surfaces have shown the contraction of the interlayer separation of the first few surface layers.[1,2] The contraction is the largest for the topmost layer and decreases rather fast for the inner layers. Among the three flat surfaces (100), (110), and (111) in a face-centered-cubic crystal the largest contraction occurs for the (110) surface; the contractions at the (100) and especially the (111) surfaces are small. Bond-breaking arguments also predict the largest relaxation for the (110) surface and smaller relaxations for the (100) and (111) surfaces since, by creation of a surface, an atom on the surface loses five nearest neighbors for the (110) surface, four for the (100) surface, and three for the (111) surface. Furthermore, the interlayer separation is smaller for the (110) surface than that for the (100) and (111) surfaces. However, all the calculations to date[3,4] based on pair potentials show an expansion of the interlayer separation for all the three surfaces, this being 14.9%, 8.6%, and 4.5%, of the interlayer separation for the (110), (100), and (111) surfaces, respectively, of Cu.[3]

Interest in the study of the properties of atomic defects at surfaces is rather high at present and interatomic potentials provide a convenient tool for simulation work. It is clearly desirable that the interatomic potentials to be used in such simulation work also yield the correct surface relaxation since, if this is not so, the calculated defect properties could be seriously in error. In this paper we neither propose an interatomic potential which will yield the right relaxations at the surface nor do we discuss the suitability or the validity of the concept of pair potentials for surfaces; pairwise potentials are already being used for defect calculations,[3,4] and are also being constructed from experimental data.[5] Instead, we propose a simplified scheme, assuming an interatomic potential or a simple analytic model of the electronic structure of a metal is available, for estimating such relaxations which avoids the need for performing elaborate relaxation calculations. This, we believe, will facilitate the selection of a pair potential for simulation work. Using this scheme we show that the interatomic potentials of the classical type, Morse, Lennard-Jones, etc., yield quite generally, by their very nature, an expansion of the interlayer separation and *not* the contraction as observed experimentally. This conclusion is independent of the number of nearest neighbors included in the calculation, except when the crystal is in equilibrium under the nearest-neighbor interactions, only in which case there is no relaxation at the surface. This result is, of course, expected on physical grounds. The minimum in the Morse or the Lennard-Jones potential lies to the right of the nearest-neighbor distance. The force exerted on an atom by its neighbors is therefore repulsive, while the second and distant neighbors exert an attractive force. By the creation of a surface, an atom in a layer just underneath the surface is left with a net attractive force normal to the surface, the normal pointing towards the crystal. The situation can be corrected only by letting the atoms on the surface move outwards, providing a corresponding increase in the net repulsive force so that there is no net force on the atom. This simple argument also shows that no such predictions can be made for the case of oscillatory potentials about the nature of relaxations since, unlike the case of Lennard-Jones and Morse potentials, the force exerted on an atom by its neighbors could be attractive or repulsive, depending upon the oscillations in the potential. The nature of the relaxations obtained in this case is thus intricately dependent upon the oscillations in the potential.

The relaxation calculation with pairwise potentials is discussed in Sec. II. In Sec. III the method has been applied to calculate the relaxations at an fcc transition-metal surface using the tight-binding model of Friedel.[6] In contrast to the case of Morse potential, we now obtain contractions for all three surfaces, as observed experimentally. This result perhaps indicates the need for using noncentral interatomic potentials for surface simulation work. Concluding remarks are given in Sec. IV.

II. CALCULATION OF THE SURFACE RELAXATION FOR AN fcc CRYSTAL

We assume for simplicity that the atomic relaxation takes place at the top surface layer only and that second and other internal layers are not much affected. This approximation seems justified from experimental observations and other theoretical calculations. Our calculations show that the error arising from this approximation is not more than a few percent in the calculated relaxation, the most error occuring when the unrelaxed interlayer separation is small.

Let $V(R_{ij})$ be the interatomic potential between the two atoms situated at the sites $\vec{R}_i$ and $\vec{R}_j$, with $\vec{R}_{ij}=\vec{R}_i-\vec{R}_j$. The origin of the coordinate system is placed at an atom on the surface and we will calculate its relaxed position. The surface is represented by the (x,y) plane irrespective of its orientation, and the Z axis is perpendicular to the surface. In the relaxed position the total force on an atom on the surface vanishes, i.e.,

$$\sum_j{}' \frac{\vec{R}_j'}{\vec{R}_j'}\frac{dV(R_j')}{dR_j'}=0\,, \tag{1}$$

where R_j' indicates the relaxed position of the jth atom, and the prime on the summation indicates that the self-interaction ($j=0$ term) has to be excluded. If we assume that there is no reconstruction of the surface, then it is easy to verify that the x and y components in Eq. (1) vanish identically due to symmetry. The only relaxation then arises normal to the surface due to the asymmetry created by the surface. Thus

$$\sum_j{}' \frac{Z_j'}{R_j'}V'(R_j')=0\,, \tag{2}$$

where Z_j' denotes the Z components of $\vec{R}_j'$ and $V'(R_j')=dV(r)/dr|_{r=R_j'}$. If the relaxations are small (~10%), then it is only the nearest-neighbor distance which is significantly changed and the second- and higher-order separations are not much affected. Setting, therefore, $\vec{R}_j'=\vec{R}_j$ ($j>2$), where $\vec{R}_j$ is the unrelaxed distance, we find that the following conditions should be satisfied for the relaxed (100), (110), and (111) surfaces, respectively,

$$\left(-\frac{\sqrt{2}\,Z}{R_1'}\right)V'(R_1')=\frac{1}{2\sqrt{2}}V'(R_2)+\frac{4}{\sqrt{3}}V'(R_3)+V'(R_4)+\frac{2}{\sqrt{5}}V'(R_5)+\frac{1}{\sqrt{6}}V'(R_6)\,, \tag{3}$$

$$-\left(\frac{4Z+a/\sqrt{2}}{3R_1'}\right)V'(R_1')=\frac{\sqrt{2}}{3}V'(R_2)+\frac{10}{3\sqrt{3}}V'(R_3)+V'(R_4)+\frac{14}{3\sqrt{5}}V'(R_5)+\frac{2}{3\sqrt{3}}V'(R_6)\,, \tag{4}$$

$$-\left(\sqrt{3/2}\,\frac{Z}{R_1'}\right)V'(R_1')=\frac{1}{\sqrt{2}}V'(R_2)+\frac{4}{\sqrt{3}}V'(R_3)+V'(R_4)+\frac{6}{\sqrt{5}}V'(R_5)+\sqrt{2/3}\,V'(R_6)\,. \tag{5}$$

In Eqs. (3)–(5) the summation has been restricted to the first six shells of neighbors; more neighbors may, however, be easily included. Z is the separation between the two topmost surface layers and depends on the surface orientation. The separation in the unrelaxed case Z_0 is $a/2$ for the (100) surface, $a/2\sqrt{2}$ for the (110) surface, and $a/\sqrt{3}$ for the (111) surface, a being the lattice constant. Thus the (110) surface layers have the smallest separation among the three surfaces considered here. Note that in Eq. (4) the Z coordinate of the nearest neighbor that lies in the second layer below the (110) surface layer has been approximated by its unrelaxed value.

Setting

$$R_1'=R_1+\delta R\,,\qquad Z=Z_0+\delta Z\,, \tag{6}$$

one easily sees that

$$\frac{\delta Z}{Z_0}=\left(\frac{R_1}{Z_0}\right)^2\left(\frac{\delta R}{R_1}\right). \tag{7}$$

Equation (7) thus shows that in this simple picture the fractional change in the interlayer separation is inversely proportional to the square of the unrelaxed separation. For a constant δR one would find the relaxation of the (111), (100), and (110) surfaces to be in the ratio 3:4:8—a trend which is roughly observed experimentally and found in most theoretical calculations. However, δR will, in general, vary from surface to surface. Nevertheless, one can see that, in this case, the (110) surface has the largest relaxation, essentially due to the small interlayer separation.

In the bulk of the crystal, the crystal stability condition should be satisfied. This requires that

$$\sum_j{}' \frac{dV(R_j)}{da} = 0 , \qquad (8)$$

where a is the lattice constant. Again restricting to the first six neighboring shells of atoms, this could be rewritten as

$$-V'(R_1) = \frac{1}{\sqrt{2}} V'(R_2) + 2\sqrt{3}\ V'(R_3) + 2V'(R_4) + 2\sqrt{5}\ V'(R_5) + \sqrt{8/3}\ V'(R_6) . \qquad (9)$$

Some remarks can now be made for the Lennard-Jones and Morse-type classical interatomic potentials. At second and higher interatomic distances, the gradients of these potentials are positive and vary monotonically. The crystal stability condition, Eq. (9), then requires that $V'(R_1)$ be negative, which in turn implies that $R_1 < R_0$, where R_0 indicates the position of the minimum in the interatomic potential. Noting the fact that the factor in large parentheses multiplying $V'(R_1')$ in Eqs. (3)–(5) is nearly unity (it is unity if $Z = Z_0$), one can see that the right-hand side of Eq. (9) is always larger than its counterpart in Eqs. (3)–(5). This implies that $V'(R_1') > V'(R_1)$, a condition which is obeyed if $R_1' > R_1$. We thus see that the interatomic potentials of the classical type are, by their very nature, constrained to yield an expansion in the interlayer separation. In the particular case when the crystal is in equilibrium under nearest-neighbor interactions only [$V'(R_j) = 0$, $j > 2$], one finds from Eqs. (3)–(5) that $V'(R_1') = V'(R_1) = 0$, so that $R_1' = R_1$ and there is no surface relaxation. For second-neighbor interactions one expects only weak relaxation for the (111) surface.

In order to verify the accuracy of this method, we have made quantitative estimates of relaxation from Eqs. (3)–(5) and (7) for the Morse potential

$$V(R) = D(e^{-2\alpha(R-R_0)} - 2e^{-\alpha(R-R_0)}) . \qquad (10)$$

Since the relaxations are small, we assume $Z = Z_0$ in Eqs. (3)–(5) in the factor multiplying $V'(R_1')$. With the parameters chosen by Wynblatt and Gjostein,[3] $\alpha = 1.3588$ Å^{-1}, $R_0 = 2.8659$ Å, and $D = 0.3429$ eV, we find $\delta Z/Z_0 = 0.185$, 0.092, 0.048 for the (110), (100), (111) surfaces, respectively, giving outward relaxation for all the three surfaces with the (110) having the largest. These are to be compared with the fully relaxed computer-generated values of 0.149, 0.086, 0.046 of Wynblatt and Gjostein.[3] Considering the fact that our method is rather simple and straightforward the agreement is quite gratifying, and it can be concluded that quite reliable estimates can be obtained of the surface relaxation from this simple procedure. The largest discrepancy occurs for the (110) surface which is expected since the adjacent planes are close together. However, if the relaxations obtained from our calculation are used to calculate new atomic positions and used in Eq. (2) to calculate relaxations, the values obtained are $\delta Z/Z_0 = 0.16$, 0.094, 0.048, which are in much better agreement with the results of Wynblatt and Gjostein. This later procedure has been used to calculate the relaxation for several fcc metals from the Morse-potential parameters given in Ref. 4 and the results are given in Table I. In all cases a positive outward relaxation is obtained and further one finds $(\delta Z/Z_0)_{110} > (\delta Z/Z_0)_{100} > (\delta Z/Z_0)_{111}$.

Equations (2)–(5) are also valid for the oscillatory potentials. However, precisely because $V'(R_j)$ has oscillations, no prediction on the nature of relaxation can be made which will now depend upon the details of the potential itself. For Harrison's[7] interatomic potential for Al obtained from a pseudopotential calculation

$$V(R) = A(\rho/R)^3 \cos(2KR + \phi) , \qquad (11)$$

where $A = 0.094$ eV, $\rho = 2.40$ Å, $K = 1.46$ Å^{-1}, and $\phi = 3.9128$ rad, we obtain $\delta Z/Z_0 \simeq 0.01$, 0.0, 0.014, for (110), (100), (111) surfaces, respectively, if the sum in Eq. (2) is restricted to 10 neighboring shells of atoms. Extending the summation to 18 neighboring shells of atoms affects the results only slightly and values of 0.012, 0.0, 0.022 are obtained. Thus Harrison's interatomic potential predicts small outward relaxation for the (110) and (111) surfaces and no relaxation for the (100) surface. Low-energy electron diffraction (LEED) experiments on Al (Ref. 1) seem also to indicate no relaxation for the (100) surface and a very small expansion ($\delta Z/Z_0 < 0.02$) for the (111) surface. However, for the (110) surface a contraction ($\delta Z/Z_0 \sim -0.05$ to -0.15) is observed, which is in disagreement with this calculation. Considering the fact that Harrison's interatomic potential is obtained from the bulk crystal calculations, this disagreement is not unexpected and indicates perhaps the necessity of including the surface screening effects and the three-body interactions.

III. BAND MODEL FOR TRANSITION METALS

The simple method used above to calculate relaxations with pairwise potentials may also be used with a model of electronic structure if the total energy can be expressed in an analytic form as a function of interatomic separation. We will demonstrate that the simple tight-binding model of transition metals proposed by Friedel[6] yields contraction of the distance between the topmost surface layer and the layer just below it for all the three surfaces. The density of states in this

TABLE I. Morse-potential constants and surface relaxation for fcc metals. Positive sign indicates an increase in the interlayer separation.

	Lattice constant a (Å)	D (eV)	α (Å^{-1})	R_0 (Å)	Relaxation $(\delta Z/Z_0) \times 100$ (100)	(110)	(111)
Cu	3.6147	0.3446	1.3921	2.838	8.2	13.4	4.0
Ag	4.0862	0.3294	1.3939	3.096	5.2	8.2	2.2
Au	4.0785	0.4826	1.6166	3.004	3.0	4.4	1.0
Ni	3.5238	0.4279	1.3917	2.793	9.0	14.8	4.4
Pd	3.8907	0.4761	1.6189	2.890	3.8	5.8	1.4
Pt	3.9239	0.7102	1.6047	2.897	2.6	3.8	1.0
Ir	3.8389	0.8435	1.6260	2.864	4.4	6.8	2.0
Rh	3.8044	0.6674	1.5423	2.875	5.4	8.6	2.6
Pb	4.9502	0.2455	1.2624	3.667	3.4	5.2	1.0

model is represented by a rectangular step function of width W and height $10/W$. The Fermi energy E_F for a metal with Z electrons in the d shell is related to the bandwidth W, and given by $E_F = W(Z-5)/10$, the zero of energy is at the center of the band and coincides in this model with the position of the atomic d levels. The cohesive energy E_d, due to the d electrons, is given by

$$E_d = \frac{W}{20} Z(10-Z)\,. \tag{12}$$

It may be noted here that the parabolic trend in the cohesive energy across a transition-metal series predicted by the model is generally observed experimentally. The bandwidth can be calculated from the second moment of the density of states through the relation

$$\mu_2 = W^2/12\,. \tag{13}$$

We now make the approximation that the second and high neighbor d-d overlap and transfer integrals can be neglected in relation to the nearest-neighbor ones. In this case μ_2 can be written[6] in terms of the average intersite hopping or transfer integrals, $\beta(R_j)$, between the atom at the origin and another one situated at $\vec{R}_j$ as

$$\mu_2 = {\sum_j}' \beta^2(R_j)\,, \tag{14}$$

where the summation extends over the nearest neighbors only and the prime indicates that the $\vec{R}_j = 0$ term is to be excluded. Combining Eqs. (12)–(14) we have

$$E_d = \frac{A}{\beta_0}\left({\sum_j}' \beta^2(R_j)\right)^{1/2} \tag{15}$$

with $A = (\sqrt{3}/10)Z(10-Z)\beta_0$, where β_0 is the value of $\beta(R)$ at $R = R_0$, the equilibrium bulk interatomic separation. Following Friedel[6] and Ducastelle[8] we assume the transfer integrals to vary exponentially in the neighborhood of R_0, i.e.,

$$\beta(R) = \beta_0 e^{-q(R-R_0)}\,, \tag{16}$$

although an R^{-n} dependence ($n \simeq 4-5$) has also been proposed.[9,10]

Equation (15) gives only the d-band bonding contribution to the cohesive energy, which increases as the interatomic separation is decreased. In transition metals this is by far the dominant term. The s-d hybridization is more difficult to treat. However, following Gelatt, Ehrenreich, and Watson[10] (GEW), let us assume that it has qualitatively the same behavior as the d-band contribution; the hybridization matrix element increases as the d-band width increases, and the hybridization contribution to the cohesive energy is largest near a half-filled d band (as is the d-band contribution), except that it does not vanish for a filled d band [the d-band contribution, in contrast, vanishes for a filled d band, cf. Eq. (12)] and instead tails with increasing valence. The detailed information on the behavior of the s-d contribution to the cohesive energy as a function of interatomic separation is not easily obtained. So we assume that this term can be included in Eq. (15) via a suitable modification of the parameters. The attractive interaction between the d shells on neighboring sites results, as discussed by GEW, in a reduction of the interatomic separation (compared to the case if the d electrons were neglected) and thus in the compression of the free-electron gas.

The stability of the lattice requires that there be a countervailing short-range repulsive force. This is provided by the compression of the free-electron gas. As the atoms are brought together to form the solid, the free-electron contribution to the cohesive energy is at first attractive since the valence charge density is pushed into a region of more attractive potential [in a nearest-neighbor simple tight-binding picture this means that the contribution from the intrasite hopping integral α_s is attractive and greater than the intersite hopping integral $\beta_s(R_{ij})$, which is repulsive]. However, as the interatomic separation is further decreased, α_s passes through a minimum (at a distance greater than the equilibrium interatomic separation) and then begins to rise. In addition, the kinetic-energy cost (contribution from β_s) of compressing the electron gas becomes dominant.

In this necessarily simplified picture, the repulsive contribution to the cohesive energy E_s in transition metals thus arises from the s electrons and is dominated by the term involving β_s. In the neighborhood of the equilibrium interatomic separation it is not unreasonable to assume that it varies as $e^{-p(R-R_0)}$ since β_s, being an interatomic hopping integral, is expected to vary approximately in this fashion. We thus write

$$E_s = B \sum_j{}' e^{-p(R_j-R_0)}, \tag{17}$$

where the constant B depends on β_s. The arguments leading to Eq. (17) are based on the tight-binding model of s electrons which, seemingly inappropriate in this case, has nevertheless been fruitfully exploited by Ching and Callaway[11] and others for the calculation of the electronic structure of both simple and transition metals. We further note that the form given by Eq. (17) for the repulsive term has also been suggested by Friedel and co-workers.[6,8,12] However, it should not be construed to represent the core-core repulsion which is negligible at separations of interest to us.

The total cohesive energy is then

$$E_c = E_d + E_s ,$$

and at equilibrium separation it has the minimum, i.e.,

$$\left.\frac{dE_c}{dR}\right|_{R=R_0} = 0 .$$

With this one obtains

$$E_c = A\left(\sum_j{}' e^{-2q(R_j-R_0)}\right)^{1/2} - \frac{A}{\sqrt{N}}\frac{q}{p}\sum_j{}' e^{-p(R_j-R_0)}, \tag{18}$$

where N is the number of nearest neighbors. Equation (18) now replaces the interaction energy, $\phi = \sum_j{}' V(R_j)$, of an atom obtained in Sec. II for interatomic potentials. Note that in contrast to the case with interatomic potentials, where the interaction energy is the direct sum of bond energies, it now depends on the bond energies in a rather complicated way. It is easily seen that Eq. (2) is now replaced by the following equation for a relaxed surface:

$$\left(\sum_j e^{-2q(R_j'-R_0)}\right)^{-1/2} \sum_j{}' \frac{Z_j'}{R_j'} e^{-2q(R_j'-R_0)} = \frac{1}{\sqrt{N}} \sum_j{}' \frac{Z_j'}{R_j'} e^{-pR_j'} . \tag{19}$$

We again calculate the relaxation of the topmost surface layer from the layer just below it assuming that the separation of all the other consecutive layers below the surface layer does not change. An atom on the (111) surface has a total of nine nearest neighbors, six on the surface and three on the layer just below it. On the (100) surface there are eight neighbors, four each on the surface and the adjacent layer. In contrast, for the (110) surface an atom has only seven nearest neighbors. Apart from having two neighbors on the first surface layer and four on the second, there is one neighbor directly below it on the third surface layer. Although the separation between the second and third layers may be assumed unchanged, the separation between the first and the third may not be because of the relaxation of the first, and this has to be taken into consideration while calculating the relaxation of the (110) surface. Setting $R_1' = R_1 + \delta R$ and $Z_1' = Z_1 + \delta Z$, where R_1' is the distance of the nearest neighbors situated on the plane just below the surface plane in the relaxed configuration, and expanding the exponentials to second order in δR in Eq. (19), the following equations for (111), (100), and (110) surfaces are obtained from which $X = \delta R/R_0$ can be determined,

$$\left(\frac{\sqrt{3}}{4}p'^2 - \frac{7}{6}q'^2\right)X^2 - \left(\frac{\sqrt{3}}{2}p' - \frac{5}{3}q'\right)X - \left(1 - \frac{\sqrt{3}}{2}\right) = 0 , \tag{20}$$

$$\left(\frac{p'^2}{\sqrt{6}} - \frac{7}{8}q'^2\right)X^2 - \left(\sqrt{2/3}\,p' - \frac{3}{2}q'\right)X - (1 - \sqrt{2/3}\,) = 0 , \tag{21}$$

$$\begin{aligned}[\sqrt{7/12}\,(3p'^2 - 8p' - 7) - (\tfrac{246}{49}\,q'^2 - 10q' - 7)]X^2 \\ - [\sqrt{7/12}\,(4p' - 7) - (\tfrac{38}{7}q' - 7)]X \\ - 3(1 - \sqrt{7/12}\,) = 0 ,\end{aligned} \tag{22}$$

where $p' = pR_0$ and $q' = qR_0$. On the basis of cohesive energy, compressibility, and elastic-constant data Ducastelle[8] has suggested the values $p' = 9$ and $q' = 3$. This gives $\delta R/R_0 = -0.0364$ -0.0458, and -0.0403 for the (111), (100), and (110) surfaces, respectively. From Eq. (7) we may calculate the fractional change in the interlayer separation $\delta Z/Z_0$, and one obtains contractions of 5.5%, 9.2%, and 16.1% for the (111), (100), and (110) surfaces, respectively. Thus the model predicts the largest contraction for the (110) surface. Note that in this model the relaxation is determined by the parameters p and q which describe essentially the short-range repulsive interaction and the hopping probability of the d electrons to a neighboring site. It may be further shown from Eqs. (20)–(22) that this model predicts contraction of the interlayer separation for all the three surfaces, not only for the values of p and q chosen above but for all resonable choices of p and q. Further, if it is assumed that p and q vary slowly across a given transition-metal series, one expects approximately the same surface relaxation for all the face-centered-cubic transition metals. LEED experiments[1] show very small relaxation for the (100) surface (+2.5% Ni, 4% Co, ~0.0 Rh) and (111) surface (−1% Ni, 2.5% Ir, ~0.0 Pt, −4.1% Cu), but a significant contraction for the (110) surface (−5% Ni, −10% Cu, Ag). The comparison with the experimental data for Ni is somewhat complicated since interatomic correlations have not been included. Nevertheless, considering the simplicity of the model employed, the results are encouraging. Further improvements, such as a better treatment of the s-d hybridization and the s-electron contribution to the cohesive energy, will be necessary before one can expect better results. The noble metals serve to further emphasize this need where d-band contribution to the cohesive energy is derived essentially from the s-d hybridization.

The model presented above is not intended to explain or to predict the contractions for all fcc metal surfaces. The model obviously does not apply to the case of Al where contractions are also observed. However, in this simple tight-binding picture the relaxations will be determined by a competition between the attractive intra-atomic (α_s) and the repulsive interatomic (β_s) s-band contributions to the cohesive energy.

IV. CONCLUSION

We have shown that the atomic relaxations on clean metal surfaces can be estimated quite accurately in a simple manner without the need for elaborate computations. Using this technique we have also shown, by taking the example of the face-centered-cubic metals, that the interatomic potentials of the classical type, Morse, Lennard-Jones, etc., yield, by their very nature, an expansion in the distance separating the top two surface layers because of the constraints built into them. No such prediction can be made *a priori* regarding potentials of the oscillating type. However, based on the oscillatory interatomic potential of Harrison, it is likely that the oscillatory interatomic potentials obtained from the bulk pseudopotential calculations may not yield the correct surface relaxation and that charge-transfer effects on the surface may have to be included. Such effects have been treated in the literature for simple metals.[13-15]

It has been shown that Friedel's tight-binding model for transition metals yields contraction in the interlayer separation of the first two surface layers as observed experimentally. This result is independent of the parameters chosen in the model and demonstrates the important role played by d electrons in surface relaxation. For a reasonable set of parameters the contraction predicted is somewhat larger than that observed experimentally.

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[1] F. Jona, J. Phys. C 11, 4271 (1978).

[2] J. Friedel, Ann. Phys. (Paris) 1, 257 (1976).

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

[4] P. G. Flahive and W. R. Graham, Surf. Sci. 91, 449 (1980).

[5] R. Casanova and T. T. Tsong, Phys. Rev. B 22, 5590 (1980).

[6] J. Friedel, in *Electrons*, Vol. I of *Physics of Metals* edited by J. M. Ziman (Pergamon, London, 1969).

[7] W. A. Harrison, *Pseudopotentials in the Theory of Solids* (Benjamin, New York, 1964).

[8] F. Ducastelle, J. Phys. (Paris) 31, 1055 (1970).

[9] D. G. Pettifor, J. Phys. C 3, 367 (1970); V. Heine, Phys. Rev. 153, 673 (1967); J. Hubbard, Proc. Phys. Soc. London 92, 921 (1967).

[10] C. D. Gelatt, Jr., H. Ehrenreich, and R. E. Watson, Phys. Rev. B 15, 1613 (1977).

[11] W. Y. Ching and J. Callaway, Phys. Rev. B 11, 1324 (1975).

[12] G. Allan and M. Lanoo, Phys. Status Solidi B 74, 409 (1976).

[13] M. W. Finnis and V. Heine, J. Phys. F 4, L37 (1974).

[14] V. Landman, R. N. Hill, and M. Mostoller, Phys. Rev. B 21, 448 (1980).

[15] M. Hietschold, G. Paasch, and I. Bartos, Phys. Status Solidi B 101, 239 (1980).