

## Equivalent-crystal theory of oscillatory surface relaxation

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The surface relaxation of the low-index planes of Ni, Cu, Ag, and Al has been computed via the method of equivalent crystals. Good agreement with experiment is obtained. The sign of the change in interlayer spacing is observed to alternate with depth in all cases. The relaxations can be simply understood as a competition between a bond compression energy and an energy which depends essentially only on distances to neighboring atoms.

A simple and yet accurate method of computing total energies and structures of defects in solids has long been desirable and in fact considerable progress has been made toward that goal.<sup>1-4</sup> We have introduced a new method<sup>5</sup> in which the total energy is computed as if each atom were in a crystal, as described below. Surface energies of a series of transition metals were computed as a function of surface grain orientation, and good agreement was obtained with the results of first-principles calculations and with experimental results.

Recently, ion scattering and low-energy electron-diffraction (LEED) studies<sup>6-18</sup> of low-index surfaces of a number of metals have indicated a relaxation in surface-layer spacings which is oscillatory in nature. This alternation with depth of the sign of the change in interlayer spacing has also been seen in surface calculations on Al,<sup>19,20</sup> Al-Ni,<sup>4</sup> and Fe alloys.<sup>21</sup>

Here we describe calculations of surface relaxations for all the low-index planes of Ni, Cu, Ag, and Al, providing the first quantitative agreement with experiment for a series of transition metals. Because of the simplicity of this new method, a simple understanding of the factors controlling the relaxation and the oscillatory character is obtained. Moreover, the accuracy obtained for interlayer relaxations bodes well for the intended use of this efficient new method for materials science phenomena such as adhesion.

The total energy  $E$  of a solid containing a defect is computed as if each atom were in an *equivalent crystal*. This single crystal is equivalent to the defect solid in the sense that it has the same total energy at the appropriate lattice constant. An exact relationship for the total energy was written<sup>5</sup> as the energy of a crystal plus a perturbation series, where the perturbing potential is the difference between the potential of the crystal and that of the defect solid. The lattice constant of the crystal is then varied until it has the same energy as the defect solid, i.e., until the perturbation series vanishes. In Ref. 5 we ultimately approximated the first- and second-order perturbation terms as  $\sum_m g(R_m, \alpha)$ , where  $R_m$  is the *distance* to the  $m$ th neighbor. This amounts to averaging over functions which depend only on distances to determine the lattice constant, and that tends to obscure anisotropic bond distortion energies. Such distortions do not occur for isotropic deformation. Here, however, we consider relaxations where, e.g., some bond lengths are expanded while others

are compressed relative to bulk values. This requires the most general approach. By far the most important distortion energy to include beyond an averaging over  $R$  is that due to bond compression. This is because of the rapid rise of the energy during compression (see Fig. 1, Ref. 22). One could keep higher-order perturbation terms to include such anisotropic compression energies. There is a simpler solution, however, within the equivalent crystal approach. We compute each bond compression energy for the defect solid as if it were the change in the cohesive energy per nearest-neighbor bond of a crystal having the same bond-length change. One can take advantage of the recent discovery<sup>22</sup> of a universal relationship between  $E$  for a single crystal and the crystal's scaled lattice constant  $a^*$ :

$$E = \Delta E [F^*(a^*) - 1] = -\Delta E (1 + a^*) e^{-a^*}. \quad (1)$$

Here  $\Delta E$  is the cohesive energy of the crystal. This leads to the following simple relationship for the surface energy  $\sigma$  as a function of interatomic spacings:

$$\sigma = (\Delta E/A) \left[ \sum_{n=1}^N F^*(a_{0n}^*) + \sum_{m=1}^M (\theta_{mn}/L_{mn}) F^*(a_{mn}^*) \right]. \quad (2)$$

Here  $A$  is the surface area,  $N$  is the number of atoms in the solid,  $\theta_{mn} = 1$  if  $a_{mn}^* \leq 0$  and  $\theta_{mn} = 0$  otherwise,  $M$  is the number of nearest neighbors of atom  $n$ ,  $L_{mn}$  is the number of nearest neighbors of atom  $m$  or  $n$ , whichever number is smaller,  $a_{mn}^* = (R_{mn}/c_1 - r_{\text{WSE}})/l$ ,  $l = \sqrt{\Delta E/(12\pi B r_{\text{WSE}})}$ ,  $B$  is the bulk modulus of the crystal,  $R_{mn}$  is the distance between atoms  $m$  and  $n$ ,  $c_1$  is the ratio of the equilibrium nearest-neighbor distance in the crystal to  $r_{\text{WSE}}$ , and  $r_{\text{WSE}}$  is the equilibrium Wigner-Seitz radius ( $3/4\pi r_{\text{WSE}}^3 \equiv$  bulk atom density). The numbers  $a_{0n}^*$  (one for each atom  $n$ ) are determined from a simple perturbation expression, as described in Ref. 5. Although the second sum in Eq. (2) is only over nearest neighbors, the energy depends on all neighbors through Eq. (1). Because of periodicity, the sum over  $n$  includes only one site for each layer, and typically  $N=6$  is more than sufficient. The evaluation of Eq. (2) is relatively trivial.

The first term on the right-hand side of Eq. (2) follows from Eqs. (3) and (8) of Ref. 5. For a single crystal,  $a_{0n}^* = 0$  for all  $n$ , and so the first term in that case is at its minimum value, which is zero. This term is positive for

surface atoms, representing an energy of excitation associated with the formation of the surface, i.e., the surface energy. The second term is the bond compressional energy computed as if it were a crystalline bond. It is zero for unrelaxed surfaces ( $a_{mn}^* = 0$ ,  $m = 1, \dots, M$ ) such as those treated in Ref. 5. Equation (2) appears to be similar in form to that used in other approaches (see, e.g., Refs. 3, 4, and 23), where the energy of an atom  $U_i$  is written as the sum of a term which depends on the local atom density  $\rho_i$  and a pairwise term:  $U_i = f(\rho_i) + \frac{1}{2} \sum_j V_{ij}$ . There are fundamental differences, however. Our first term includes electronic screening, which is an effect of crucial importance in surface calculations. Screening enters naturally via perturbation theory.<sup>5</sup> Our second term is not a pair potential. This term is of the form of a cohesive energy, and is zero for isotropic deformation or when bonds are not compressed, while pair potentials are nonzero in both cases. Finally, the accuracy of our defect energy computations can be arbitrarily improved through the systematic perturbation theory framework.<sup>5</sup> This framework not only leads to improved accuracy but also clarifies the nature of the approximations that are made. Such understanding is important in applying the theory to new systems.

It remains to list values of the four experimental input parameters:  $\Delta E$ ,  $r_{WSE}$ ,  $l$ , and  $\alpha$ . The first three are given in Tables I and II of Ref. 24. Values of  $\alpha$  in  $\text{\AA}^{-1}$  for Cu, Ag, Ni, and Al are 2.944, 2.105, 3.336, and 3.015, respectively, as determined from vacancy formation energies.

The interlayer spacings are found by total-energy minimization. That is,  $\sigma$  is minimized as a function of all interplanar spacings. The results for all low-index planes of Al, Ag, Ni, and Cu are given in Table I. All surfaces were fully relaxed in that interplanar spacings  $\Delta d_{12}$  through  $\Delta d_{45}$  were varied for all surfaces. If the change in spacing was  $\leq 0.3\%$ , the result was not included in the table, with the exception of  $\Delta d_{45}$  for Al(110), because there is experimental data for the latter.

First, note the size of the changes in interplanar spacings. Take, for example, the case of Ni(110), where the surface layer relaxation  $= \Delta d_{12} = -0.084 \text{ \AA}$ . The energy change is also rather small, with total-energy change associated with the relaxation of all the layers of Ni(110) being  $51 \text{ ergs/cm}^2$  or  $28 \text{ meV}$  per surface unit cell. Such small changes provide a severe test for any theory.

Second, compare the experimental values, where available, with the predictions. Note that in nearly every case the experimental values, including error bar ranges, overlap each other. Also one can see that in almost every case, the predictions are within the experimental error bars. Only two predictions are significantly outside the error bars,  $\Delta d_{12}$  for the (111) surfaces of Cu and Al. This provides more evidence of the progress in the field of surface spectroscopy. Further, that sort of accuracy ( $\sim 0.01 \text{ \AA}$ ) is as good or better than one might hope to obtain using today's first-principles methods, even if one were willing to expend the relatively large amount of computer time required to reproduce the results of Table I from first principles.

Third, note that the predicted  $\Delta d_{12} \leq 0$  for every surface. This is also true of every experimental result except

that for Al(111) (Ref. 16). The measured expansion for Al(111) is small, however. The driving force for the reduction of  $d_{12}$  is the first term of Eq. (2). Because surface atoms are missing neighbors, the equivalent crystal for atoms in the surface layer has a lattice constant which is larger than the bulk equilibrium value, i.e.,  $a_{01}^* > 0$ . This leads to an excitation (surface) energy through the first term of Eq. (2) which is, for example,  $0.94 \text{ eV}$  for Al(110),  $0.66 \text{ eV}$  for Al(100), and  $0.41 \text{ eV}$  for Al(111) in units of energy per surface unit cell. The surface layer moves toward the second layer in order to lower this excitation energy by increasing the density of atoms around each surface atom. Because there are five missing nearest neighbors around each (110) surface atom, four missing for each (100) surface atom, and three missing for (111) surface atoms, the surface layers would have to move a large fraction of the interplanar spacing in order to obtain volume-averaged density in their vicinities comparable to that found in the bulk. Those large relaxations do not occur because some nearest-neighbor bonds are compressed during the relaxation so that the second term in Eq. (2) constrains the relaxation. So the price of having the local atom density increase to come closer to the bulk density is a compression of some nearest-neighbor bonds below the bulk nearest-neighbor spacing. This occurs because of the anisotropy associated with the surface. For relaxation of an isotropically expanded bulk solid toward equilibrium density, all nearest-neighbor distances are equal to each other and  $\geq$  the equilibrium spacing. We see that this is fundamentally different from what is happening in the surface.

Next, one can see that in every case the sign of the spacing change alternates with depth. This damped, oscillatory relaxation has been observed before as noted earlier. Here we see that it has a somewhat broad applicability. This can be understood in terms of Eqs. (1) and (2) as follows. Let us consider first the somewhat simpler cases of the (100) and (111) surfaces. The spacing  $d_{12}$  decreases primarily until the rate of decrease of the density energy of layer 1 [first term, Eq. (2)] equals the rate of increase of bond compression energies between layers 1 and 2 [second term, Eq. (2)], as discussed above. At the same time, however, the density energy of layer 2 is increased by a small amount by the decrease in  $d_{12}$ , for example, by  $1.9 \text{ meV}$  for Al(111). This increase is enough to force an increase in  $d_{23}$ . The increase in  $d_{23}$  will continue until the rate of decrease in the density energy of plane 2 equals the rate of increase of density energy of plane 3. The increase in  $d_{23}$  is smaller than the decrease in  $d_{12}$  because the original increase in the density energy of layer 2 is much smaller than the original increase of the density energy of layer 1 due to the creation of the surface [ $1.9 \text{ meV}$  vs  $410 \text{ meV}$  for Al(111)]. This is because before the relaxation, layer 2 is at the minimum of the universal relation  $F^*(a^*)$  where  $[dF^*(a^*)/da^*]_{a_{02}^*} = 0$ , while layer 1 is at lower density so that  $F^*(a^*)$  has a significant slope at  $a^* = a_{01}^*$ . This kind of mechanism continues on into the bulk for alternating plane pairs, and hence the damped oscillatory relaxation. Sometimes the mechanism is a bit more complicated. The increase in  $d_{23}$  can lead to a further decrease in  $d_{12}$  by lowering the den-

TABLE I. Percentage changes in interlayer spacings due to relaxation. Calculated absolute changes are also given in Å for reference.

Element	$\Delta d_{n,n+1}$	Changes in spacing (%)		Experiment	Technique
		Theory (Abs. changes, Å)			
Cu(110)	$\Delta d_{12}$	-6.5	(-0.083)	$-8.5 \pm 0.6$ $-7.5 \pm 1.5$	LEED (Ref. 9) Ion scattering (Ref. 15)
	$\Delta d_{23}$	+2.7	(+0.034)	$+2.3 \pm 0.8$ $+2.5 \pm 1.5$	LEED (Ref. 9) Ion scattering (Ref. 15)
Cu(100)	$\Delta d_{12}$	-3.5	(-0.063)	$-2.1 \pm 1.7$ $-1.1 \pm 0.4$	LEED (Ref. 12) LEED (Ref. 11)
	$\Delta d_{23}$	+1.6	(+0.029)	$+0.45 \pm 1.7$ $+1.7 \pm 0.6$	LEED (Ref. 12) LEED (Ref. 11)
Cu(111)	$\Delta d_{12}$	-2.8	(-0.058)	$-0.7 \pm 0.5$	LEED (Ref. 14)
Ag(110)	$\Delta d_{12}$	-5.4	(-0.078)	-5.7 $-7.8 \pm 2.5$	LEED (Ref. 11) Ion scattering (Ref. 10)
	$\Delta d_{23}$	+2.4	(+0.035)	+2.2 $+4.3 \pm 2.5$	LEED (Ref. 11) Ion scattering (Ref. 10)
Ag(100)	$\Delta d_{12}$	-2.9	(-0.059)		
	$\Delta d_{23}$	+1.4	(+0.029)		
Ag(111)	$\Delta d_{12}$	-2.3	(-0.054)		
	$\Delta d_{23}$	+1.1	(+0.026)		
Ni(110)	$\Delta d_{12}$	-6.8	(-0.084)	$-8.7 \pm 0.5$ $-9.0 \pm 1.0$	LEED (Ref. 13) Ion scattering (Ref. 8)
	$\Delta d_{23}$	+3.2	(+0.040)	$+3.0 \pm 0.6$ $+3.5 \pm 1.5$	LEED (Ref. 13) Ion scattering (Ref. 8)
Ni(100)	$\Delta d_{12}$	-3.7	(-0.065)	$-3.2 \pm 0.5$	Ion scattering (Ref. 17)
	$\Delta d_{23}$	+1.7	(+0.030)		
Ni(111)	$\Delta d_{12}$	-2.9	(-0.059)	$-1.2 \pm 1.2$	LEED (Ref. 18)
	$\Delta d_{23}$	+1.4	(+0.028)		
Al(110)	$\Delta d_{12}$	-10.1	(-0.14)	$-8.6 \pm 0.8$ $-8.5 \pm 1.0$	LEED (Ref. 7) LEED (Ref. 6)
	$\Delta d_{23}$	+4.8	(+0.068)	$+5.0 \pm 1.1$ $+5.5 \pm 1.1$	LEED (Ref. 7) LEED (Ref. 6)
	$\Delta d_{34}$	-0.4	(-0.006)	$-1.6 \pm 1.2$ $+2.2 \pm 1.3$	LEED (Ref. 7) LEED (Ref. 6)
	$\Delta d_{45}$	0.0	(0.0)	$+0.1 \pm 1.3$ $+1.6 \pm 1.6$	LEED (Ref. 7) LEED (Ref. 6)
Al(100)	$\Delta d_{12}$	-5.0	(-0.10)		
	$\Delta d_{23}$	+2.1	(+0.042)		
Al(111)	$\Delta d_{12}$	-3.6	(-0.084)	$+0.9 \pm 0.5$	LEED (Ref. 16)
	$\Delta d_{23}$	+1.8	(+0.042)		

sity energy of plane 2. This is because the density energy of plane 2, while much smaller than the bond compression energy between planes 1 and 2, can nevertheless also inhibit the decrease of  $d_{12}$  to some extent. Now let us consider the (110) surfaces. The effects discussed above for the (111) and (100) surfaces are also involved in the (110) relaxation, but for the latter there is a nearest neighbor two planes away in the (110) direction. Thus when  $d_{12}$  decreases, there is a bond compression energy associated with layer 3 as well as a density energy increase for layer 3. As  $d_{23}$  increases, lowering this bond compression energy and the density energies of planes 2 and 3,  $d_{12}$  can then decrease significantly more. This oscillatory mechanism continues on into the bulk.

Note that the magnitudes of relaxation percentages are ordered as (110) > (100) > (111). One might presume that this is due to the excitation (surface) energies before relaxation being in that same order as noted above. However, that is not the dominant effect. Rather, it can be understood in terms of nearest-neighbor geometries. The distances between planes are ordered as (111) > (100) > (110). For a given percentage change in interplanar spacing, the smaller the distance between planes the smaller the percentage change in nearest-neighbor distance because of the bond angle relative to the normal to the plane. It is the change in the nearest-neighbor distance that dominates the change in both terms of Eq. (2). Thus the smaller the interplanar spacing

the slower the change in surface energy with change in interplanar spacing. This is the primary reason for the ordering of the relaxation percentages. One must add that the energies of Eq. (2) include all-neighbor interactions through Eq. (1), as noted earlier, but the nearest neighbors tend to dominate the energetics.

Finally, we consider the order of the magnitudes of relaxation percentages, which is  $Al > Ni > Cu > Ag$ . Note this is the order of predicted relaxations and, although there is scatter in the experimental results, this is sensibly the order in experimental results also. If one orders according to *decreasing* elastic constants, one finds  $Al > Ag > Cu > Ni$ . Thus the usual measure of stiffness of a material fails here, with the exception of Al. This is

perhaps not surprising, because in creating a surface the energies are moved well away from equilibrium values where elastic constants apply. Thus the ordering arises from the energetics of a defect far from equilibrium and it is not simply related to equilibrium properties.

In summary, the relaxations of a number of surfaces have been computed simply via a new method which treats each atom as if it were in an equivalent crystal. The agreement with experimental results is good. A simple understanding of the direction of relaxations, including the oscillatory behavior, is obtained. Because of the ease of applicability and accuracy of this new method, it holds considerable promise for the understanding of more complex materials science phenomena.

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