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Multilayer lattice relaxation at metal surfaces

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Relaxation at simple metal surfaces is studied via minimizaton of the total energy of a semi-infinite crystal. Systematic analysis of the contributions to the total energy demonstrates the importance of a proper, three-dimensional treatment of electronic response. Multilayer relaxation is shown to be essential for quantitative predictions. Results for the low-index faces of Na and for Al(110) are presented. Good agreement with detailed low-energy electron diffraction data for oscillatory multilayer relaxation in Al(110) is obtained.

Metal surface structural information is essential for the understanding and elucidation of a large number of surface phenomena. Consequently, major efforts have been devoted in recent years to the development of surface structure experimental probes and their analysis. Progress in the formulation and implementation of theories of structurally predictive capability has been limited, hindered by the complexity of the problem. Such theories, however, are of great importance since they can provide structural input parameters to be employed in the analysis of data and reveal the nature of the forces (and their relative contributions) which govern the atomic arrangement and in particular structural modifications (relaxation and reconstruction) which are expected (and indeed observed) at the surface region of materials. These observations have led to the recent formulation[1] of a simple electrostatic model which predicted, semiquantitatively, multilayer surface relaxation in both fcc and bcc materials dependent upon surface crystallographic orientation and other material parameters. The existence of multilayer relaxation phenomena has since been verified by several careful examinations of low-energy electron diffraction (LEED) for several systems [e.g., Al(110),[2] Cu(110),[2,3] V(100),[4] Re($0\bar{1}01$) (Ref. 4)]. In this Rapid Communication we report the first results of calculations based on *total energy minimization* which provide *quantitative* estimates of metal surface structural parameters, elucidate the nature of forces governing the structure, multilayer relaxation in particular, and improve upon previous theories in several ways. We illustrate the theory by applying it to the low-index surfaces of Na and to Al(110) and obtain good agreement with recent experimental data.

The total energy E_T is expressed as the sum of the ground-state electron gas energy E_0, the Madelung electrostatic energy E_M of point ions in the presence of a semi-infinite negative neutralizing background, the interaction of point ions with the surface dipole layer $E_{\rm DL}$, and of the Hartree and band-structure contributions, $E_{\rm H}$ and $E_{\rm BS}$, respectively:

$$E_T\{\lambda_n\} = E_0 + E_M\{\lambda_n\} + E_{\rm DL}\{\lambda_n\} + E_{\rm H}\{\lambda_n\} + E_{\rm BS}\{\lambda_n\} \ . \tag{1}$$

In our calculation we retain the explicit dependence of the total energy on the crystalline structure. In particular the last four terms depend on layer positions, $z_n^{\lambda} = (n - \frac{1}{2} + \lambda_n)d$, $n = 1, 2, \ldots$, where d is the layer spacing in the bulk and $\lambda_n d$ is the deviation from the truncated bulk location of layer n. E_M and $E_{\rm BS}$ depend in addition on intralayer structure and on interlayer registry [$\Delta\vec{R}$ will denote the shift in origin of the two-dimensional (2D) lattice between adjacent layers, and is characteristic to the exposed face]. The total energy is minimized with respect to λ_n, $n = 1, 2, \ldots, N_s$.

In the evaluation of the Hartree and band-structure energies we use the local form of the Heine-Abarenkov model pseudopotential,

$$V_P(R,z) = \begin{cases} ZV_C(R,z), & R^2+z^2 > r_c^2 \\ -Ze^2u_c/r_c, & R^2+z^2 \leq r_c^2 \end{cases} \tag{2}$$

where

$$V_C(R,z) = -e^2(R^2+z^2)^{-1/2} \ ,$$

Z is the valence, and u_c and r_c are the pseudopotential parameters (chosen[5] to fit the bulk compressibility and lattice parameter and used to determine vacancy formation energies). [For Na ($r_s = 3.931a_0$), $r_c = 2.076a_0$ and $u_c = 0.3079$; for Al ($r_s = 2.064a_0$), $r_c = 1.388a_0$ and $u_c = 0.3894$.]

The dipole-layer energy is given by

$$E_{\rm DL}\{\lambda_n\} = Z \sum_n \int d^2R \int dz\, [\rho^e(z) - \rho^+(z)]\, V_C(R, z - z_n^{\lambda}) \ , \tag{3}$$

where $\vec{R}$ is a 2D vector in the surface plane. The Hartree contribution,

$$E_{\mathrm{H}}\{\lambda_n\} = \sum_n \int d^2R \int dz\, \rho^e(z)\,[V_P(R,z-z_n^\lambda) - ZV_c(R,z-z_n^\lambda)]\ , \tag{4}$$

constitutes together with E_{DL} the first-order correction to the electron-jellium system (E_0) due to the replacement of the positive background by the ionic pseudopotentials. In Eqs. (3) and (4) the background density is denoted by $\rho^+(z) = (3/4\pi r_s^3)\theta(z)$, where $\theta(z)$ is the Heaviside step function, and the ground-state electron density in the presence of $\rho^+(z)$ is $\rho^e(z)$. In our calculations, we employ the Lang and Kohn[6] electron density.

In the most primitive model (the PITB model) the system consists of point ions in the presence of a truncated bulk electron density, $E_T\{\lambda_n\} = E_0 + E_M\{\lambda_n\}$. The addition of the dipole-layer and Hartree contributions (the DLH model) significantly improves the physical picture and predictive value by including a more realistic description of the inhomogeneous surface conduction-electron density and its first-order interaction energy with the ions.

However, the DLH model of surface relaxation (sometimes termed the "frozen profile model") which has been used previously to predict multilayer relaxation[1] does not include the response of the electrons to the presence of the ions. Attempts to further improve on this model have all been limited to single-layer relaxation[7–9] and in certian of these an approximate one-dimensional potential has been used.[9] As is demonstrated by our results and their comparison to experimental data both multilayer relaxation and the full three-dimensional nature of the ionic system must be included in a proper and quantitative treatment of surface relaxation.

The band-structure energy (second order in the pseudopotentials) can be written as

$$E_{\mathrm{BS}}\{\lambda_n\} = \tfrac{1}{2} \sum_{\vec{G}} \sum_{n,m} [\exp(i\vec{G}\cdot\Delta\vec{R})]^{n-m} \int dz\, \rho_n^\lambda(G;z)\, W_m^\lambda(G;z)\ , \tag{5}$$

where $\vec{G}$ is the 2D reciprocal lattice vector, and $W_m^\lambda(G;z)$ is the 2D Fourier transform of

$$W_m^\lambda(R,z) = V_P(R,z-z_m^\lambda) - \frac{1}{N_A} \int d^2R' \int_{(m-1)d}^{md} dz' \rho^+(z')\, V_C(|\vec{R}-\vec{R}'|, z-z') \tag{6}$$

(N_A is the number of ions in a layer). The induced (screening) electron density is linearly related to W_n^λ through

$$\rho_n^\lambda(G;z) = \int dz'\, \alpha_0(G;z,z')\,[W_n^\lambda(G;z') + \phi_n^\lambda(G;z')]\ , \tag{7a}$$

$$\phi_n^\lambda(G;z) = \int dz'\, g(G;z,z')\, V_C(G;z-z')\, \rho_n^\lambda(G;z')\ , \tag{7b}$$

where α_0 is the random-phase approximation polarizability and correlation and exchange are included via the local field correction g. The solution of Eqs. (7) is facilitated by using the infinite barrier response model,[10,11] and by the ansatz $g(G;z,z') = g(G;|z-z'|)$ (Ref. 12).

Including only the $\vec{G}=0$ contribution to E_{BS} [Eq. (5)] is equivalent to a one-dimensional treatment of the electron response obtained by averaging the ionic potential over the layers (we denote this 1D electron response model of E_T by DLHBS0, to contrast with the model, denoted by DLHBS, in which the complete E_{BS} is included).

Results for the surface structures of the low-index faces of Na and of Al(110) obtained via minimization of the total energies corresponding to the various models and those obtained by other theories, as well as values obtained from experimental analyses, are summarized in Table I. Percent changes, $\Delta_{n,n+1}$, of the interlayer distance between layers n and $n+1$ from the bulk value, for differing numbers N_s of layers allowed to relax, are given. Inspection of the results shows that relaxation is more pronounced for the open faces, and that multilayer relaxation is essential in all the models and systems considered. Note, for example, the change in sign in Δ_{12} obtained via DLHBS0 for Na(100) and Na(111) when allowing for multilayer relaxation. [Although for $N_s=6$ the relaxations did not yet converge for Na(111), calculations with $N_s=9$ in the PITB and DLH models did not significantly change the values of Δ_{12} through Δ_{34}.] We find damped oscillatory relaxations with a period equal to the stacking period [three for Na(111) and two for the other surfaces]. Comparison of the results of the DLH and PITB models illustrates that the interaction of the ions with the inhomogeneous surface electron density tends to decrease relaxations, resulting from a reduced deviation of the first layer from its position relative to the bulk. The importance of the full inclusion of the band-structure contribution is vividly illustrated by comparing the results of the DLHBS and DLHBS0 models. Agreement with detailed experimental results[2] for Al(110) is dramatically improved by using the complete band structure (DLHBS) and allowing multilayer relaxation. These results also demonstrate

TABLE I. Surface relaxations for the low-index faces of Na and for Al(110) expressed in percent changes $\Delta_{n,n+1}$ of the interlayer distance between layers n and $n+1$ from the bulk value. N_s is the number of layers allowed to relax. The larger value of N_s is the one for which convergence is obtained. Negative values of $\Delta_{n,n+1}$ indicate contraction of the interlayer spacing. Results for the various models (see text) are shown in order of increasing complexity. Note the effect of the multilayer relaxations and their oscillatory character.

Model	Na(100)				Na(110)			
	N_s	Δ_{12}	Δ_{23}	Δ_{34}	N_s	Δ_{12}	Δ_{23}	Δ_{34}
PITB	1	−7.0			1	−0.69		
	9	−10.8	4.0	−1.2	9	−0.72	0.03	−0
DLH	1	−1.3			1	0.29		
	9	−1.9	0.7	−0.4	9	0.15	0.12	0.01
DLHBS0	1	1.2			1	1.0		
	4	−0.4	1.2	0.4	3	0.09	0.25	0.82
DLHBS	1	−3.6			1	−0.08		
	4	−2.7	0.7	−1.0	3	−0.16	0.08	0.01
Expt.						≈0 (Ref. 13)		
Ref. 8	1	−2			1	0.0		
Ref. 9	1	+1			1	−5.0		

Model	Na(111)							Al(110)			
	N_s	Δ_{12}	Δ_{23}	Δ_{34}	Δ_{45}	Δ_{56}	Δ_{67}	N_s	Δ_{12}	Δ_{23}	Δ_{34}
PITB	1	−34						1	−11		
	9	−67	−10	53	−40	6	18	9	−26	16	−8
DLH	1	−13						1	−4		
	9	+3	−35	27	0	−15	11	9	−12	8	−4
DLHBS0	1	−10						1	−5		
	6	4	−32	24	0	−12	10	6	−14	9	−2
DLHBS	1	−20						1	−14		
	6	−8	−29	23	−2	−11	8	6	−10	4	−3
Expt.									−8.4 ±0.8 (Ref. 2)	4.9 ±1.0	−1.6 ±1.1
Ref. 8											
Ref. 9	1	−12.5							Could not find minimum		

that the multilayer relaxation phenomena predicted by the simple electrostatic models[1] (PITB and DLH) do occur when electron response is included properly, and is necessary for quantitative theoretical structural predictions. These observations resolve questions raised by several authors related to this issue.[8,9] Finally, we note the magnitude[14] and sequence of predicted relaxations for Na(111) which would provide an interesting challenge for experimental endeavor.

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[1]U. Landman, R. N. Hill, and M. Mostoller, Phys. Rev. B 21, 448 (1980).
[2]D. L. Adams *et al.*, Phys. Rev. Lett. 49, 669 (1982); H. B. Nielsen, J. N. Andersen, L. Petersen, and D. L. Adams, J. Phys. C 15, L1113 (1982).
[3]H. L. Davis and J. R. Noonan, J. Vac. Sci. Technol. 20, 842 (1982).
[4]V. Jensen, J. N. Andersen, H. B. Nielsen, and D. L. Adams, Surf. Sci. 116, 66 (1982); H. L. Davis and D. M. Zehner, J. Vac. Sci. Technol. 17, 190 (1980).
[5]Z. D. Popovic, J. P. Carbotte, and G. R. Piercy, J. Phys. F 4, 351 (1974).
[6]N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).
[7]G. P. Alldredge and L. K. Kleiman, J. Phys. F 4, L207 (1974).
[8]K. -P. Bohnen, Surf. Sci. 115, L96 (1982).
[9]J. P. Perdew, Phys. Rev. B 25, 6291 (1982).
[10]R. N. Barnett, R. P. Barrera, C. L. Cleveland, and U. Landman (unpublished). This paper contains a comprehensive discussion of the response model and of the method of solution of the coupled integral equations (7).
[11]P. W. Lert and J. H. Weare, J. Phys. C 11, 1865 (1978).
[12]K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B 1, 1044 (1970).
[13]S. Anderson, J. B. Pendry, and P. M. Echenique, Surf. Sci. 65, 539 (1977).
[14]The results for bcc (111) surfaces given in Ref. 1 are in error due to a mistake in the input 2D reciprocal lattice used in the calculation of the Madelung energy.