Multilayer Relaxation of Interlayer Registry and Spacing at High-Index Metal Surfaces

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Oscillatory multilayer relaxation of both interlayer spacing and registry at certain high-index metal surfaces is predicted via minimization of a simple model for the total energy of a semi-infinite crystal. Results for the (210) and (211) surfaces of bcc and fcc simple metals indicate that the relaxation parallel to the surface plane moves the surface layers toward more symmetrical configurations with respect to adjacent layers.

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Theoretical predictions[1-3] and recent analysis of low-energy electron-diffraction data[4] have revealed damped oscillatory relaxations of the interlayer distances for the low-index surfaces of several materials. While quantitative agreement [see results for Al(110) in Refs. 1 and 2] between the theoretical predictions based on minimization of total energy of the semi-infinite crystal required the inclusion of a realistic treatment of the electronic response to variations in the atomic positions, the qualitative features of the multilayer relaxation phenomena were described already at the level of a "frozen profile" model[3] (see also Refs. 1 and 2) where band-structure contributions to the total energy are neglected. Motivated by these results and by the interest which they have created we embarked upon investigations of the structure of more open (higher-index) surfaces of fcc and bcc simple metals. The major prediction resulting from our studies is that these less symmetrical surfaces undergo multilayer oscillatory interlayer registry relaxation [which may be termed (1×1) reconstruction] in addition to multilayer oscillatory relaxation of interlayer spacings. These results are obtained via minimization of the total-energy expression which depends explicitly upon the atomic positions, with three-dimensional relaxations [with no change of the two-dimensional (2D) unit cell] allowed. Following a brief description of the physical model we present results for the (211) and (210) surfaces of Na (bcc) and Al (fcc).

To facilitate our discussion we specify the position of the ith ion in layer l by

$$\vec{r}_{i,l}=\vec{R}_i+l\,\Delta\vec{R}+\alpha_{1,l}\vec{A}_1+\alpha_{2,l}\vec{A}_2+[z_0+(l-\tfrac{1}{2}+\lambda_l)d]\hat{z},\quad l=1,2,\ldots,\tag{1}$$

where the capital letters are 2D vectors in the surface (x-y) plane, and $\hat{z}$ is a unit vector perpendicular to the surface plane and directed into the semi-infinite crystal; $\vec{R}_i$ describes the 2D lattice of a layer, $\vec{R}_i=i_1\vec{A}_1+i_2\vec{A}_2$, where i_1 and i_2 are integers, $\vec{A}_1$ and $\vec{A}_2$ are the 2D primitive translation vectors; $\Delta\vec{R}$ is the shift in origin (registry shift) between the 2D lattices of adjacent layers; and d is the bulk layer spacing. The quantities $\vec{A}_1$, $\vec{A}_2$, d, and $\Delta\vec{R}$ are given in Table I for fcc and bcc (211) and (210) surfaces.[5] The difference between the equilibrium and truncated bulk location of the ions in layer l is given by

$$\Delta\vec{r}_l=\alpha_{1,l}\vec{A}_1+\alpha_{2,l}\vec{A}_2+\lambda_l d\hat{z}\,.$$

To find the equilibrium configuration of the semi-infinite metal it is necessary to minimize the total energy with respect to $\alpha_{1,l}$, $\alpha_{2,l}$, and λ_l for all $l>0$. We assume that $\Delta\vec{r}_l=\vec{0}$ for $l>N_s$ and use the method of steepest descent[2] to minimize the total energy in this configuration space.

To obtain the results discussed in this paper we have used two models for the total energy of

TABLE I. Surface structure parameters: $\vec{A}_1$ and $\vec{A}_2$ are the 2D primitive translation vectors, d is the distance between adjacent layers, $\Delta\vec{R}$ is the registry shift between consecutive layers, a is the cubic cell edge length, and N_R is the layer stacking sequence period.

Parameter	bcc (211)	fcc (211)
$\vec{A}_1$	$\sqrt{2}\,a\hat{x}$	$(1/\sqrt{2})a\hat{x}$
$\vec{A}_2$	$-(\sqrt{3}/2)a\hat{y}$	$-\sqrt{3}a\hat{y}$
d	$a/\sqrt{6}$	$a/2\sqrt{6}$
$\Delta\vec{R}$	$\vec{A}_1/2+2\vec{A}_2/3$	$\vec{A}_1/2+\vec{A}_2/3$
N_R	6	6
	bcc (210)	fcc (210)
$\vec{A}_1$	$a\hat{x}$	$a\hat{x}$
$\vec{A}_2$	$-\sqrt{5}a\hat{y}$	$-a/2\hat{x}-(\sqrt{5}/2)a\hat{y}$
d	$a/2\sqrt{5}$	$a/2\sqrt{5}$
$\Delta\vec{R}$	$\vec{A}_1/2+7\vec{A}_2/10$	$7\vec{A}_1/10+2\vec{A}_2/5$
N_R	10	10

the system; both models neglect the response of the conduction electrostatic, or "frozen profile," models.[1-3] The simplest model is the point ion, truncated bulk electron density (PITB) model in which the ions are represented by point positive charges and the conduction-electron density is simply a truncated uniform bulk density, i.e.,

$$\rho^e(z)=\rho^+(z)\equiv(\tfrac{3}{4}\pi r_s{}^3)\theta(z-z_0)$$

where r_s is the electron density parameter. The total energy in the PITB model is

$$E_T{}^{\mathrm{PITB}}(\{\alpha_{1l}\},\{\alpha_{2l}\},\{\lambda_l\})=E_0{}^{\mathrm{TB}}+E_{\mathrm{M}}(\{\alpha_{1l}\},\{\alpha_{2l}\},\{\lambda_l\}), \tag{2}$$

where $E_0{}^{\mathrm{TB}}$ is the energy of the conduction electrons in the presence of a neutralizing positive background density $\rho^+(z)$, and E_{M} is the Madelung energy, i.e., the electrostatic energy of point ions in the presence of a neutralizing negative background $[\rho^+(z)]$.

In the second model, the dipole layer, Hartree energy (DLH) model, the conduction-electron density, $\rho^e(z)$, is taken to be the Lang-Kohn[6] "jellium" system ground-state density, and the interaction of the ions with this electron density is obtained with use of the local form of the Heine-Abarenkov model pseudopotential (pseudopotential parameters are given in Ref. 1). The total energy in the DLH model is

$$E_T{}^{\mathrm{DLH}}(\{\alpha_{1l}\},\{\alpha_{2l}\},\{\lambda_l\})=E_0{}^{\mathrm{LK}}+E_{\mathrm{DL}}(\{\lambda_l\})+E_{\mathrm{H}}(\{\lambda_l\})+E_{\mathrm{M}}(\{\alpha_{1l}\},\{\alpha_{2l}\},\{\lambda_l\}), \tag{3}$$

where $E_0{}^{\mathrm{LK}}$ is the jellium system electronic ground-state energy, E_{DL} is the interaction of point ions with the "surface dipole layer," i.e., with $[\rho^e(z)-\rho^+(z)]$, and E_{H} is the Hartree energy which together with E_{DL} constitutes the first-order correction to the jellium system energy, $E_0{}^{\mathrm{LK}}$, due to replacing the positive background with the ionic pseudopotentials.[1,2]

Results obtained from the DLH-model-relaxation-(1×1)-reconstruction calculations for the (211) and (210) surfaces of Na and Al are presented in Tables II and III, respectively. These results were obtained with the number of layers in the surface region, N_s, equal to the layer stacking sequence period, N_R. We find that, as in the relaxation results for low-index surfaces,[1-3] multilayer oscillatory shifts in the relative ionic positions occur. Note that the positions of ions relative to the neighboring ions (rather than the positions relative to the unrelaxed bulk configuration) are the physically significant and experimentally measurable quantities. Since calculations performed with several values of $N_s<N_R$ have shown a dependence of the relaxed configuration on N_s, a multilayer calculation is necessary

TABLE II. Relaxation/reconstruction results of the DLH model for Na (211) and (210) surfaces. The change in position of ions in layer l is given by $\delta\vec{r}_l=\alpha_{1,l}\vec{A}_1+\alpha_{2,l}\vec{A}_2+\lambda_l d\hat{z}$. The quantities $\Delta\alpha_{1,l}$, $\Delta\alpha_{2,l}$, and $\Delta\lambda_l$ give the relative shift in the positions of ions in adjacent layers, defined by $\Delta\alpha_{1,l}=(\alpha_{1,l+1}-\alpha_{1,l})\times100\%$, etc. The values of $\Delta\alpha_{1,l}$ and $\Delta\alpha_{2,l}$ which bring layer l into the position of highest 2D symmetry with respect to layer $l+1$ are as follows: $\Delta\alpha_{1,l}=0$ and $\Delta\alpha_{2,l}=-16.7\%$ for (211) layers; $\Delta\alpha_{1,l}=0$ and $\Delta\alpha_{2,l}=-20\%$ for (210) layers.

Layer (l)	$\alpha_{1,l}$	$\alpha_{2,l}$	λ_l	$\Delta\alpha_{1,l}$ (%)	$\Delta\alpha_{2,l}$ (%)	$\Delta\lambda_l$ (%)
			Na (211)			
1	0	0.009	0.115	0	−10.8	−21.1
2	0	−0.100	−0.096	0	11.9	16.0
3	0	0.019	0.064	0	−5.6	−11.1
4	0	−0.037	−0.047	0	4.6	7.6
5	0	0.009	0.029	0	−2.2	−4.5
6	0	−0.013	−0.016	0	1.3	1.6
			Na (210)			
1	0	0.011	0.513	0	−4.0	−41.1
2	0	−0.029	0.102	0	0.7	−65.4
3	0	−0.022	−0.552	0	4.1	88.3
4	0	0.019	0.331	0	−2.1	−31.2
5	0	−0.003	0.019	0	−0.3	−29.9

TABLE III. Relaxation/reconstruction results of the DLH model for Al (211) and (210) surfaces. See the caption for Table II. The values of $\Delta\alpha_{1,l}$ and $\Delta\alpha_{2,l}$ which bring layer l into the position of highest 2D symmetry with respect to layer $l+1$ are as follows: $\Delta\alpha_{1,l} = 0$ and $\Delta\alpha_{2,l} = 16.7\%$ for (211) layers; $\Delta\alpha_{1,l} = -3.3\%$ and $\Delta\alpha_{2,l} = -6.7\%$ for (210) layers.

Layer (l)	$\alpha_{1,l}$	$\alpha_{2,l}$	λ_l	$\Delta\alpha_{1,l}$ (%)	$\Delta\alpha_{2,l}$ (%)	$\Delta\lambda_l$ (%)
			Al (211)			
1	0	−0.017	0.449	0	4.0	−57.7
2	0	0.023	−0.128	0	−3.1	−15.6
3	0	−0.009	−0.284	0	1.0	51.4
4	0	0.001	0.230	0	0.9	−28.2
5	0	0.010	−0.052	0	−1.5	−1.4
6	0	−0.004	−0.065	0	0.4	6.5
			Al (210)			
1	0.021	0.042	0.232	−0.5	−1.0	−27.7
2	0.016	0.032	−0.045	−2.0	−4.0	−10.2
3	−0.004	−0.008	−0.147	0.7	1.5	25.9
4	0.003	0.00	0.112	−0.2	−0.4	−12.8
5	0.001	0.002	−0.016	−0.4	−0.8	−2.4

to get reliable results. In general, the interlayer registry relaxation shifts the first and second layers toward a more symmetric position with respect to each other; however, since the interlayer coupling extends beyond adjacent layers, this is not necessarily true for the deeper layers. Although the relaxation-reconstruction parameters α_{1l}, α_{2l}, and λ_l have not in all cases converged to zero near the bottom of the surface region ($l = N_s$), the near-surface-layer results are not significantly affected when N_s is decreased by one or two layers.

In the PITB model the relaxed configuration is independent of material properties (density, ion valence Z, and pseudopotential parameters), and depends only on the crystal structure (fcc or bcc). Results obtained from the PITB model are not presented because of space limitations. In general, the relaxation in this model is much larger than the DLH-model results but the qualitative nature of the relaxed configuration is the same. Thus it is shown that, as in the case of normal relaxation of low-index surfaces,[1-3] the Madelung energy term is primarily responsible for establishing the trends. The principal combined effect of the dipole-layer and Hartree terms is to reduce the magnitude of the (inward) displacement of the surface layer. Thus, through coupling between layers and between the surface normal and parallel displacements, all components of $\Delta\vec{r}_l$ for each layer are reduced by the inclusion of the dipole-layer and Hartree terms.

A further improvement of the model will consist of the inclusion of electron response contributions. However, in our previous systematic study of normal relaxations of low-index surfaces[1,2] we found that the neglect of electron response did not significantly effect the principal relaxation trends. Indeed, after the completion of the work reported here, we have been kindly provided with the results of a low-energy electron-diffraction analysis of the Fe(211) surface in which similar relaxation-reconstruction trends were found.[7]

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[1] R. N. Barnett, Uzi Landman, and C. L. Cleveland, Phys. Rev. B 27, 6534 (1983).

[2] R. N. Barnett, C. L. Cleveland, and Uzi Landman, Phys. Rev. B 28, 1685 (1983).

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

[4] 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); H. L. Davis and J. R. Noonan, J. Vac. Sci. Technol. 20, 842 (1982); 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] A useful reference is John F. Nicholas, *An Atlas of Models of Crystal Surfaces* (Gordon and Breach, New York, 1965).

[6] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

[7] J. Sokolov, H. D. Shih, U. Bardi, F. Jona, and P. M. Marcus, to be published.