

## External-Charge-Induced Surface Reconstruction on Ag(110)

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The effect of external fields on the structural and electronic properties of Ag(110) is investigated using local-density-functional theory. We find that Ag(110) undergoes a  $(1 \times 2)$  missing-row reconstruction as an excess charge of  $\approx 0.05$  electron per surface atom is added onto the surface. Our result supports an electron-donation mechanism for the alkali-metals-induced reconstruction on the (110) surface of the  $3d$  and  $4d$  fcc metals. The surface interlayer spacings are found to be insensitive to the applied field in the absence of field-induced surface reconstruction.

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The effect of an electric field on the structural and electronic properties of a metal surface are of interest for the understanding of a wide variety of surface phenomena: electric field effects in scanning tunneling microscopy (STM) and field-ion microscopy (FIM), changes of surface properties with alkali-metals adsorption (e.g., work function lowering, enhancement in catalytic activity, adsorbate-induced reconstructions), as well as the properties of metal-electrolyte interface. Although recent developments in the first-principles total-energy calculations have made it possible to determine the electronic and geometric structures of the clean crystalline surfaces, little is known about the surface energetics and the changes of surface properties in the presence of external fields. In this paper, we present results from a local-density-functional (LDF) study of the structural and electronic properties of Ag(110) under an applied electric field. We find that the surface undergoes a missing-row reconstruction as a small amount ( $\approx 0.05$  electron per surface atom) of excess charge is transferred to (or induced on) the surface. On the other hand, in the absence of field-induced surface reconstruction, we find that the magnitude of surface interlayer (and intralayer) spacings are insensitive to the applied field. Our finding explains the success of surface structural probes (STM and FIM) in resolving the structure of clean metallic surfaces even though a finite field is present at the surface.

One of the intriguing features of the fcc noble and transition metals is the occurrence of the  $(1 \times 2)$  missing-row reconstruction on the clean (110) surface of the  $5d$  fcc metals.<sup>1,2</sup> While a  $(1 \times 1)$  surface structure is stable on the corresponding isoelectronic  $4d$  and  $3d$  metal surfaces, the missing-row reconstruction can be induced with the adsorption of submonolayer amounts of alkali metals<sup>3-6</sup> [e.g., the reconstruction is induced with less than 0.1 monolayer of K on Ag(110)]. Examination of the fcc  $(1 \times 1)$  surface layer shows close-packed rows formed by surface atoms with their nearest-neighbor

bonds arranged entirely along the row direction (i.e.,  $\langle \bar{1}10 \rangle$ ), and only weak second-nearest-neighbor interactions coupling neighboring rows. In the missing-row-reconstructed geometry, alternate  $\langle \bar{1}10 \rangle$  atomic rows are removed. This reconstructed structure can occur at the fcc (110) surface without breaking extra nearest-neighbor bonds on the surface; on the other hand, the resultant structure provides a larger surface facet area for the delocalized  $s,p$  electron to spread out to lower their kinetic energy. This geometry-related mechanism has been suggested previously by Ho and Bohnen.<sup>2</sup> Earlier, mechanisms such as the attractive force from  $s,p$  electrons,<sup>7</sup> and a competition between the attractive pair interactions and the repulsive three-body interactions,<sup>8</sup> have also been proposed. By comparison, the mechanism of the alkali-metals-induced reconstruction is less well understood. Although the fact that the reconstruction induced by submonolayer amounts of adsorbed alkali metals suggests a long-range mechanism, the induced reconstruction has also been attributed to local adsorbate-substrate bonding effects.<sup>9</sup> However, in the calculation of Ref. 9 the surface electron density is modeled by overlapping atomic charge densities which, by definition, excludes all effects of electron transfer. In this context, the study of Ag(110) under electric fields is interesting, since it not only allows us to examine the effect of induced charge on the surface properties, but makes it possible to decouple electron-donation effects from local bonding interactions which enables us to investigate the mechanism of the alkali-metals-induced reconstruction.

In this investigation the Ag(110) surface is described by periodic slabs seven atom-layer thick and separated by a seven-layer vacuum. For alkali metal/Ag(110) systems, we model the adsorbed alkali-metal ions by an effective external charge with a planar Gaussian-type distribution in the vacuum region. The external-charge profile is chosen to have a negligible overlap with the surface electronic density so that the only effect of the

external charge is that of an applied electric field. Thus the present model is also applicable to metal-electrolyte interfaces in the capacitancelike double-layer region. The magnitude of the external charge reflects the coverage of the adsorbate and the number of electrons in the system is adjusted to maintain an overall electrical neutrality. The LDF equations are solved self-consistently by use of the norm-conserving pseudopotential,<sup>10</sup> mixed-basis method.<sup>11</sup> Relaxed surface geometries for both the (1×1) and the (1×2) structures are fully optimized by calculating forces<sup>12</sup> acting on the atoms using the Hellmann-Feynman theorem. As a reference system we use the unrelaxed bulk-truncated geometry which has a calculated lattice constant of 4.10 Å.<sup>2</sup> The electronic wave functions are expanded in a mixed set with five localized *d* orbitals per atom in numerical form and plane waves with a cutoff energy of 10.5 Ry.

First, we consider the structure of the clean surface. We find that the (1×1) surface has a lower surface energy than that of the (1×2) surface. However, the energy difference between these two structures is small [ $\approx 2$  mRy/(surface atom)], indicating a near instability of Ag(110) towards reconstruction. Consistent with experimental data<sup>13,14</sup> our calculation shows that multilayer relaxation occurs near the surface region with  $\Delta d_{12} = -7.4\%$ ,  $\Delta d_{23} = 2.0\%$ , and  $\Delta d_{34} = -0.7\%$  (where  $\Delta d_{ij}$  indicates the percentage change in the interlayer spacing between the *i* and *j* layers from that of the bulk). The metastable (1×2) missing-row structure has a larger surface corrugation leading to larger atomic relaxations. The equilibrium surface geometry of the (1×2) structure determined from our calculation shows contraction of  $d_{12}$  and  $d_{23}$  ( $\Delta d_{12} = -9\%$  and  $\Delta d_{23} = -1\%$ ), a lateral displacement of atoms in the second layer ( $=0.03$  Å), and the rippling of the third atomic layer ( $\Delta z_3 = 4\%$ ). The atoms are displaced in the direction similar to the case of (1×2) Au(110).<sup>15</sup> However, the magnitude of the atomic relaxations on Ag(110) are about 50% of those of Au(110), despite the softer bulk modulus of Ag. This difference can be attributed to the lower value of the interstitial charge density in Ag leading to a weaker driving dipole force for the surface relaxations (discussion below).

Now consider the surface in the presence of an applied electric field. We present in Fig. 1 the surface energy<sup>16</sup> for both the (1×1) and the (1×2) structures as they depend upon the magnitude of induced electron charge on the surface (here a positive value of induced charge indicates electrons are induced on the surface such as the case of alkali-metals adsorption on metals). The surface energy in the presence of a field decreases as the number of induced surface electrons increases, since the electrons near the surface region experience the attractive potential from external positive ions. The charged surface undergoes a structural transformation from (1×1) to (1×2) as the number of induced electrons reaches a value of  $q_c \approx 0.05$  e/(surface atom) (or  $-6.5 \mu\text{C}/\text{cm}^2$ ,

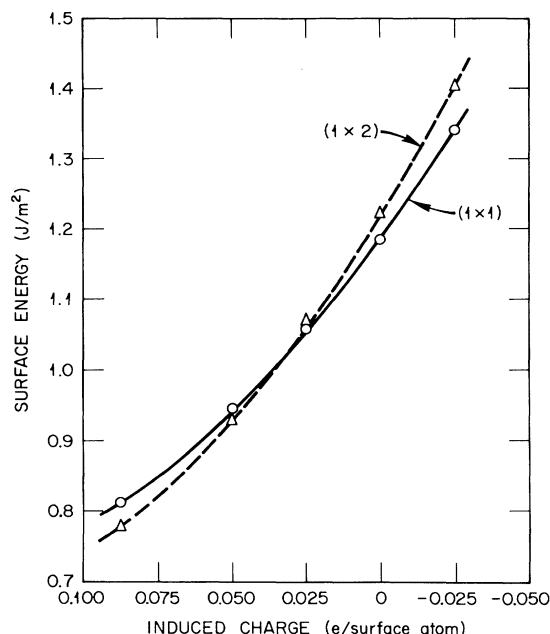


FIG. 1. Surface energies in the presence of a field for both the (1×1) and the (1×2) structures as they vary with induced charge on the surface. A positive value of induced charge indicates excess electrons are induced.

which corresponds to a field strength of  $\sim 10^7$  V/cm). The calculated  $q_c$  value is in good agreement with experiments,<sup>3,4</sup> where it is observed that submonolayer amounts of alkali metals can stabilize a reconstructed (1×2) Ag(110) surface. Our result suggests that the mechanism of the alkali-metals-induced reconstructions on the 3*d* and 4*d* fcc metal (110) surfaces operates mainly through an electron-donation effect caused by an increase in surface electron concentration donated from the adsorbed alkali-metal atoms. Since the corresponding induced surface charge density of  $q_c = -6.5 \mu\text{C}/\text{cm}^2$  can be achieved quite easily in normal electrodes, the missing-row reconstruction can also be stabilized at the fcc metals-electrolyte interface. On the other hand, the surface energy in the presence of a field increases and the (1×1) surface structure becomes even more favored over the (1×2) structure as electrons are removed from the surface (Fig. 1). It is interesting to note that the adsorption of electronegative atoms can stabilize the (1×1) structure on the fcc 5*d* metal surfaces [e.g., O/Ir(110); the clean Ir(110) surface has a (1×2) structure].<sup>17</sup> This kind of "electron acceptor" effect can be understood qualitatively in terms of our present results.

Significantly, we find that the effect of external fields (within the range of electric fields we have studied) causes negligible change in the surface structural parameters from those of the corresponding clean (1×1) and (1×2) structures (e.g., less than 0.1% in the interlayer spacings). To examine the local field in the metal, we

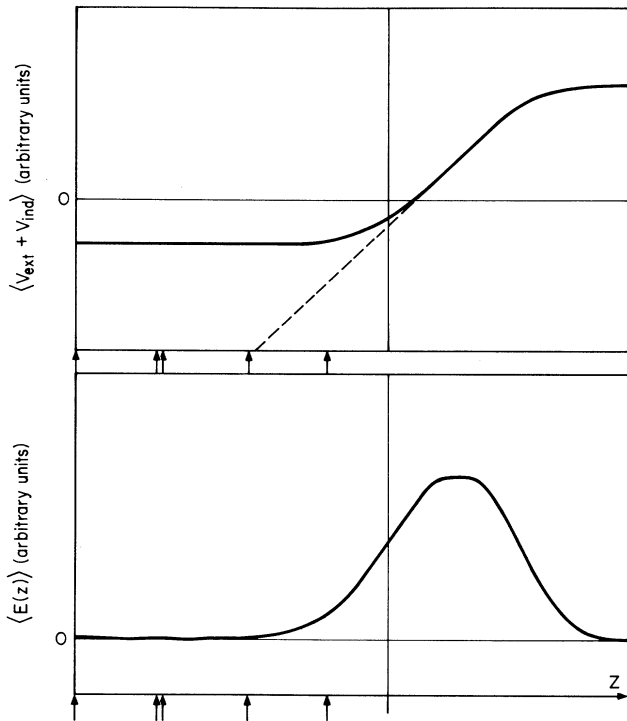


FIG. 2. Planar averaged screened external potential (upper panel) and electric field (lower panel) as functions of distance perpendicular to the surface for the  $(1 \times 2)$  surface. For reference, the dashed line represents the applied external potential. The arrows indicate the positions of the atomic planes and the vertical line is the position of the surface.

show in Fig. 2 the screened external potential and the corresponding electric field averaged parallel to the surface as a function of distance perpendicular to the surface for the  $(1 \times 2)$  structure. The external field is rapidly screened in the metal with a screening length of about one atomic layer even for the open  $(1 \times 2)$  structure. Thus the external charge perturbs the metal through the local electric field which is present and localized near the surface dipole region. Our calculated values of the inter-layer spacings of the  $(1 \times 2)$  structure are in excellent agreement with recent measurements<sup>4</sup> on K/Ag(110) (i.e.,  $\Delta d_{12} = -9\%$  and  $\Delta d_{23} = -1\%$ ). Our finding of structural insensitivity to the external fields also explains the success of certain experimental techniques (e.g., FIM, STM, etc.) in resolving the structure of clean metallic surfaces even though a finite field (which is inherent in the probing techniques) is present at the surface.

Figure 3 presents contour plots of the induced charge on the cubic  $(1\bar{1}2)$  plane (i.e., side view of the slab) of a charged surface which simulates the case of alkali-metals adsorption. The solid (dotted) contours indicate regions of increased (decreased) electrons. As shown, the induced charge is delocalized with mainly  $s, p$ -like

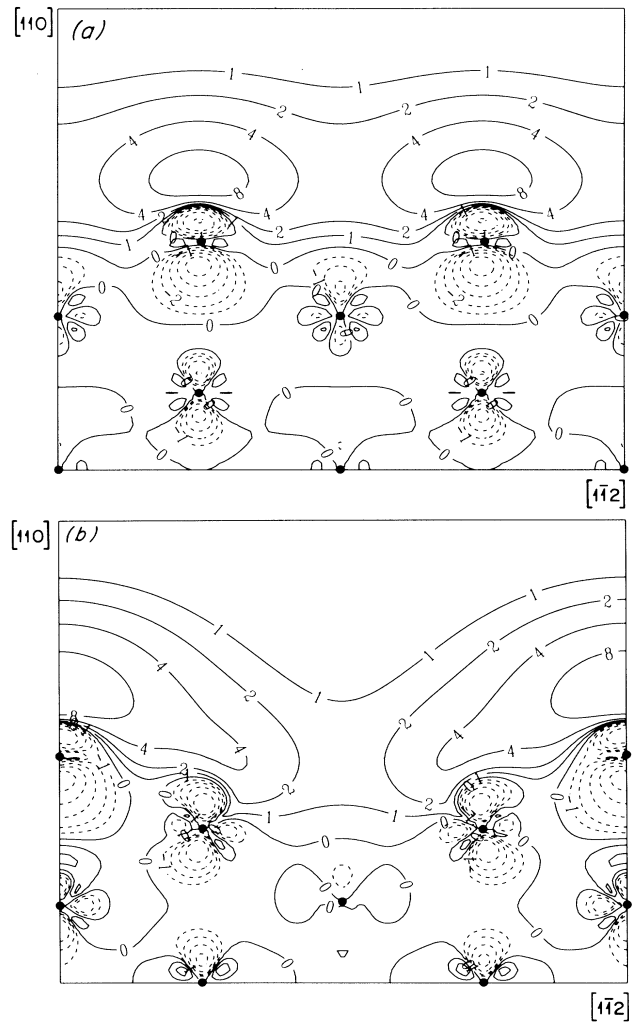


FIG. 3. Induced charge distribution of a charged surface (excess electrons) for (a) the  $(1 \times 1)$  and (b) the  $(1 \times 2)$  structures. Density plotted for the upper half of the Ag(110) slab in units of  $1 \times 10^{-4} e/a.u.$

character (which reflects the charge character of the lowest unoccupied surface state). Furthermore, a charge polarization develops about the atomic sites, and the induced electrons are mostly localized above the surface atomic plane and in the interstitial region. By comparison, the  $(1 \times 2)$  structure has a larger surface facet area and the corresponding induced charge distribution is smoother (i.e., more extended) than that of the  $(1 \times 1)$  structure. Thus the mechanism behind the missing-row reconstruction is a combination of the unique  $(110)$  surface geometry and the tendency for the  $s, p$  wave functions to spread out near the surface (under the constraint that the lowering in the kinetic energy overcomes the rise in the surface potential energy as rows of atoms are removed). An increase in density of surface delocalized electrons favors a reconstructed surface, since the lower-

ing in the kinetic energy becomes increasingly dominant in determining the relative stability of surface structures. Our calculation lends support to the theory of Ho and Bohnen<sup>2</sup> on the Au(110) surface reconstruction.

Finally, we should point out that a major difference between Au and Ag involves the more prominent relativistic effect for  $5d$  metals.<sup>18</sup> Relativistic effects enhance the  $s,p-d$  hybridization, and consequently, increase the density of delocalized electrons in the interstitial region. Thus relativistic effects lead to a stronger bonding, a larger  $s,p$  compression, and the reconstruction on the clean Au surface. The difference in the interstitial charge density between Au and Ag also manifests in the notable difference in the magnitude of atomic relaxations near the surface region; i.e., the dipole force from the delocalized electrons is less pronounced for Ag. Furthermore, the difference in the clean surface structure between Pt and Pd and between Ir and Rh can also be explained in terms of the same mechanism—a stronger  $s,p-d$  hybridization and the buildup of delocalized electrons in the interstitial region for  $5d$  metals.

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<sup>16</sup>Note that the surface energy in the presence of a field is not the absolute energy of the surface energy, since it includes both the self-energy of the external charge and interaction with the surface-induced charge. However, the energy difference between the  $(1\times 1)$  and the  $(1\times 2)$  structures is a true relevant quantity.

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