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Model for the $c(2 \times 2)$ structure induced by K on Au(110)

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We propose a new model for the $c(2 \times 2)$ structure observed in the adsorption of K on the Au(110) surface. The equilibrium geometry and structural properties are predicted from first-principles total-energy calculations. The results indicate that our model has a lower energy than a previously proposed model.

The (110) surfaces of fcc $5d$ metals Ir, Pt, and Au exhibit (1×2) reconstructions[1] that have been identified as having geometries in which alternate rows of surface atoms along the close-packed ($1\bar{1}0$) direction are removed, forming the "missing-row" structure. Missing-row reconstructions are not observed in the corresponding $3d$ and $4d$ fcc metal (110) surfaces but can be induced by depositing a small dosage of alkali-metal atoms.[2] Alkali-metal atoms can also induce further substrate constructions on Au(110) [e.g., (1×3) and (1×5) patterns are observed upon Cs deposition[3]]. Hence, it is believed that electron-donating species promote the missing-row reconstruction on this class of metal surfaces. Detailed theoretical investigations examining the physical mechanism driving the missing-row reconstruction have also indicated that the missing-row geometry is stabilized by increasing the electron density at the surface.[1,4]

Recently, the adsorption of K on Au(110) and other fcc (110) surfaces has been studied by low-energy electron diffraction (LEED) experiments[5] over a wide range of temperatures and K coverages as prototypes for alkali-metal-induced surface reconstructions. For the case of the Au(110) surface, the observations can be summarized briefly as follows:[5] The (1×2) LEED pattern is preserved if K is deposited at low temperatures (~ 100 K) and low K coverages (< 0.5). The experiments also found an increase in the background intensity and the formation of a series of "streaks" along [001] direction. This is interpreted as K atoms occupying the "furrows" of the missing rows of the Au atoms on the surface. Heating the surface to high temperatures (~ 875 K) produces a (1×3) structure at a coverage of about 0.1 monolayer. At moderately high temperatures (~ 400 K) and at half a monolayer coverage, a $c(2 \times 2)$ LEED pattern is observed. It is interpreted by the experimentalists as the removal of the (1×2) missing-row reconstruction by the K adatoms, so that the LEED pattern corresponds to the formation of an ordered $c(2 \times 2)$ overlayer of K atoms on top of an unreconstructed Au(110) (1×1) surface [Fig. 1(b)]. This interpretation was supported by subsequent "effective-medium" calculations.[6] However, this model is against the general observed trend[2] that alkali-metal absorption promotes missing-row-type structures. In addition, our experience based on previous investigations[1] on the stability of the missing-row versus the ideal (1×1) geometry indicates that addition of alkali adatoms to the surface should favor a more corrugated structure for the Au atoms. Hence, we propose an alternative model which is consistent with the LEED pattern observed experimentally.

Initially at low coverage, the K adatoms donate some of their electrons to the surface, making the original missing-row geometry even more stable relative to the (1×1) surface.[1] The positive K ions are attracted by the negatively charged surface and are positioned in the furrows of the missing rows. This gives rise to the LEED pattern observed at low coverages.[5,6] When the K coverage reaches half a monolayer, the K atoms "fill up" the furrows of the missing rows on the Au(110) surface at low temperature (~ 100 K) [Fig. 1(a)]. At high coverages, the positive ions are forced close together in the furrows. This configuration will become energetically unfavorable because of the high electrostatic energy associated with atoms of the same charge sitting on the same close-packed
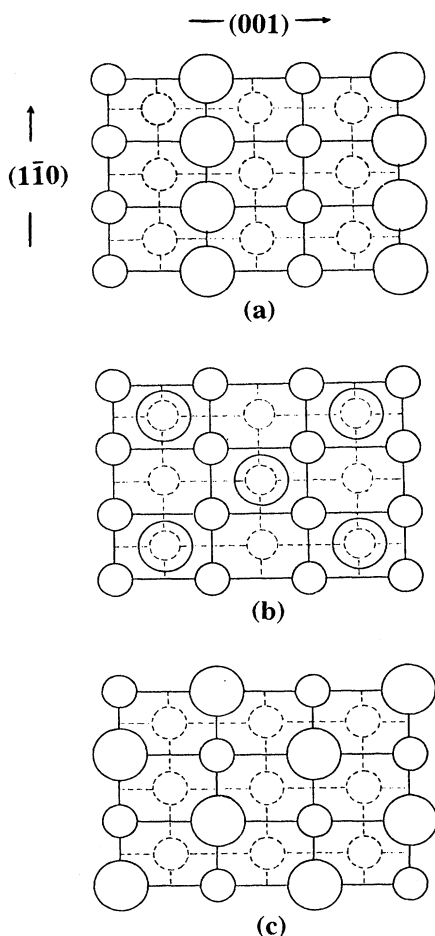
— (001) —

(1̄10)

(a)

(b)

(c)

FIG. 1. Schematic top views of (a) model A: At half mono-layer coverage and low temperature, K occupies "furrows" of the Au(110) missing rows; (b) model B: the $c(2\times2)$ K on (1×1) Au(110) surface model adopted by Ref. 5; (c) model C: alternate rows of surface atoms in model A shifted by one registry in the [001] direction to form a $c(2\times2)$ array of K and Au surface atoms. In all the figures, the larger circles represent K atoms, smaller circles Au atoms in the top layer, and dotted circles Au atoms in the second layer.

rows. The situation can be relieved by shifting alternate rows of surface atoms (Au and K together) along a [001] direction (perpendicular to the close-packed [1̄10] direction) by one row so that both the K atoms and the surface Au atoms form a $c(2\times2)$ pattern [Fig. 1(c)]. This arrangement disrupts the close-packed Au-Au rows on the surface, but the broken Au—Au bonds are replaced by Au—K bonds. Since it is known that K and Au form alloys,[7] such a replacement might not be energetically unfavorable. However, objections to this model can be raised based on the sizes of the atoms. At low coverage, the electron donation from K to the surface is quite complete so that, with an ionic radius of 1.33 Å, the K ion fits very well into the positions of the missing Au atoms (the atomic radius of Au is 1.45 Å). At high coverages, one expects less charge transfer per K atom to the surface and the size of the K atom to be closer to its atomic radius of

2.38 Å, and it may be questioned whether this large size of the K atoms can be accommodated in a top layer containing both K and Au atoms.

In order to solve the structure of the $c(2\times2)$ K on the Au(110) surface, first-principles self-consistent total-energy calculations are performed to determine the equilibrium atomic positions and the total energies of the two models to select the one with the lowest energy. The calculations are done within the density-functional formalism[8] with the Hedin-Lundqvist[9] form of exchange correlation. The methods used are similar to our previous studies of the structural and vibrational properties of the Au(110) surface.[1,4] Norm-conserving pseudopotentials[10] are used and the "partial core correction"[11] is implemented for K, which has a fairly big core. The Bloch functions are expanded in a mixed basis set[12] containing both plane waves (up to a cutoff of 12 Ry) and Gaussian orbitals centered on the Au atoms. A periodic slab geometry is employed with seven layers of Au separated by a vacuum region (thickness equal to five Au layers). Electronic wave functions are computed on a grid of 18 k points in the irreducible Brillouin zone. We consider three models: the low-temperature metastable structure (with K in furrows), the model proposed by experimentalists [$c(2\times2)$ K on Au(110) (1×1)], and our shifted-row model. They will be referred to as models A, B, and C, respectively, in the paper and are schematically shown in Figs. 1(a)–1(c). Each model is fully relaxed to its equilibrium lowest-energy configuration by computing the Hellmann-Feynman forces acting on the atoms.

We calculate for models A, B, and C the heats of adsorption per K atom, which we define to be the energy gain per K atom as half a monolayer of K atoms are put onto a fully relaxed (1×2) missing-row Au(110) surface and react to form the corresponding surface structure. The heats of adsorption are found to be 2.13, 2.40, and 2.67 eV/K atom for the equilibrium configurations of models A, B, and C, respectively. Model A (the low-temperature configuration with K in furrows) with its large electrostatic repulsion is the most unstable of the three models. The model with the lowest energy is our proposed shifted-row model (model C). We also note that these differences in energies between the different geometries are much bigger than the energy differences between the reconstructed and unreconstructed clean Au(110) surfaces.[4]

The structural parameters associated with the fully relaxed, lowest-energy configurations of the three models considered are summarized in Table I. We first note that the geometries of models B and C are sufficiently different that they should be easily distinguished by experimental techniques such as LEED (with I-V analysis) and ion scattering. Our model (model C) is characterized by a substantial contraction of the Au top interlayer spacing (d_{12}) by about 16% and a slight expansion of the second Au interlayer spacing (d_{23}) by about 5%. There is a buckling in the third Au layer with those Au atoms directly beneath the K atoms displaced towards the surface by 3.5% from the average third-layer position and those beneath the top-layer Au atoms displaced inward by the same amount. We note that the magnitudes of these re-

TABLE I: Calculated properties of half-monolayer K on Au(110) for model A, the low-temperature metastable structure with K in missing-row furrows; model B, $c(2 \times 2)$K overlayer on Au(110) (1×1); and model C, our proposed "shifted-row" model. d_{12} and d_{23} are the percentage changes in the first and second Au interlayer distances, respectively (the negative sign means contraction), and the buckling of the third Au layer (second layer for model B) is measured from the average position of the layer. K_z is the vertical distance of the K atoms above the top Au layer. The Au—K bond length is the nearest-neighbor K-Au distance. For model A, Au atoms in the second layer are nearest to K atoms.

	A	B	C
Au—K bond length (Å)	3.25	3.22	3.08
d_{12}	−11%	−4%	−16%
d_{23}	4%	5%	5%
Buckling	7%	1%	3.5%
K_z (Å)	0.83	2.04	1.08
Heat of adsorption (eV)	2.13	2.40	2.67

laxations are very similar to those found in the clean (1×2) missing-row Au(110) surface.[4] The K atoms are positioned at 1.08 Å above the Au top layer with Au-K nearest-neighbor (NN) distances of 3.08, 3.39, and 3.76 Å for Au atoms in the top, second, and third layers, respectively. This gives an average K-Au distance of 3.35 Å. Taking the radius of Au to be 1.45 Å, this gives the size of the K atom to be about 1.9 Å, which is midway between the ionic and the atomic radii. We may view model C as having half the Au atoms on a Au(110) (1×1) surface being substituted by K and the K atoms have to pop up because of their larger atomic sizes.

For model B, the relaxations are generally smaller. The top interlayer distance is contracted by only 4% and the buckling in the second Au layer is very small ($\sim 1\%$), with those Au atoms directly beneath the K atoms displaced slightly towards the bulk. The K atoms are 2.04 Å above the Au top layer, and hence quite a bit higher above the Au surface than those in model C, and have a slightly longer Au-K NN distance of 3.22 Å for atoms in the top Au layer and a Au-K distance of 3.43 Å for the Au atom directly below the K atom. Inspection of charge-density plots (see Fig. 2 for model C) reveals that for both models B and C, the K atomic cores are immersed in a sea of electrons that has little corrugation, covering the Au substrate. Hence, the bonding is essentially metallic. Our results show that K adsorption causes a substantial reduction of work function from a calculated value 5.5 eV for the clean (1×2) surface to 2.5 and 2.15 eV in models C and B, respectively. Work-function decreases of comparable magnitudes have been observed for Cs on Ag(110).[13]

In summary, we have proposed a structural model for the $c(2 \times 2)$ K/Au (110) surface. The model is conceived from physical considerations of minimizing the Coulomb repulsion between the K ions. Accurate first-principles calculations show that this new model is substantially
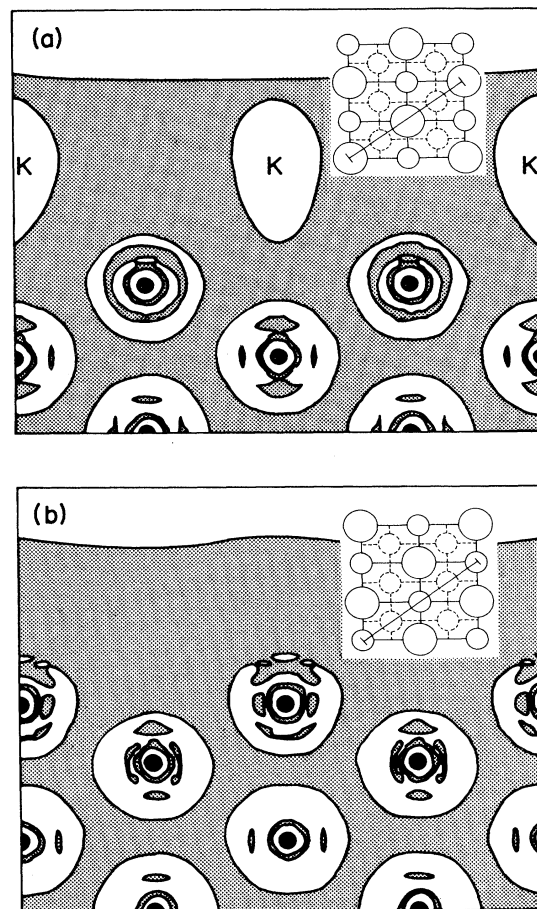

FIG. 2. Charge-density difference between the K-Au system and the superposition of Au atomic charge densities. Both (a) and (b) are for model C (shifted-row model), shown as cross sections of vertical planes [perpendicular to the (110) surface] cut along the lines shown in the inset, with plane (a) containing K adatoms. Shaded areas represent excess electrons, while blank areas have either no charge or an electron deficiency.

lower in energy than the previously proposed model. Structural parameters are predicted, which can be checked experimentally.

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