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Adsorption-site investigation of Rb/Cu(111) using the x-ray standing-wave method

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We have carried out a back reflection x-ray standing-wave investigation to study the adsorbate-substrate bond length and bonding site for the system Rb/Cu(111). Our low-energy electron diffraction study showed an ordered (2×2) phase for one monolayer of Rb on Cu(111) ($\theta=0.25$). By measuring both the (111) and ($11\bar{1}$) Bragg reflections at this coverage, we determine the Rb adsorption to be in the top site. We observe a high degree of order in the Rb overlayer perpendicular to the surface, with large disorder parallel to the surface.

I. INTRODUCTION

The adsorption of alkali atoms on metal surfaces has for a long time been the subject of both experimental and theoretical studies.¹ The interest in these systems is due in large part to the expectation that the alkalis serve as good model systems for studying metal adsorption and the metallization of overlayers on surfaces. The study of the geometry of alkali-metal adsorbates and alkali-induced changes in the substrate structure for alkalis adsorbed on metal surfaces has revealed surprising results in the past few years.²⁻⁹ For one, it was previously assumed that alkalis adsorb in high-coordination sites on low index, atomically flat metal surfaces due to their simple electronic structure. However, recent experimental evidence has shown that alkali adsorbates occupy top sites in several cases.²⁻⁹ In addition, in these top-site studies the effective hard-sphere radius of the adsorbed alkali is much smaller than its metallic radius. This implies that understanding of these chemisorption systems is not yet complete.

We have performed a low-energy electron diffraction (LEED) study for the Rb/Cu(111) system at room temperature.¹⁰ We found an ordered (2×2) phase for one monolayer of Rb on Cu(111), suggesting a single site of occupation. This observation makes this system a good candidate for investigation with the x-ray standing-wave technique. In this paper we report detailed measurements of a structural study of Rb adsorption on Cu(111) using back reflection x-ray standing waves (BRXSW). The sensitivity of this technique to adsorbate positions has been previously discussed by Woodruff *et al.*¹¹

During dynamical Bragg diffraction from a single crystal, the coherently coupled incident and reflected x-ray plane waves interfere to set up a standing-wave field parallel to and having the same spatial periodicity as the diffraction planes. By scanning (in angle or energy)

through the finite range of the total reflectivity condition, the phase of this standing wave field shifts continuously relative to the atomic scattering planes. By measuring a yield characteristic of an adsorbate excited by the standing-wave field, such as Auger, photoemission, or x-ray fluorescence, the atom's position relative to the diffraction planes can be determined.¹¹⁻¹⁷ By combining results of standing-wave measurements using sets of diffraction planes that are not parallel, the adsorbate's bonding site can also be determined by simple geometric triangulation.¹⁴ In the present paper we have performed triangulation measurements which allow us to determine the Rb bonding site unambiguously.

II. EXPERIMENT

The experiments reported below were performed on beam line X24A at the National Synchrotron Light Source at Brookhaven National Laboratory. The beamline is UHV compatible to allow windowless operation for improved flux at low photon energies. X-ray photons from the storage ring were monochromatized using a Si(111) double-crystal assembly and focused onto the sample by a toroidal nickel-coated quartz mirror.¹⁸ The UHV chamber attached to this beamline was equipped with a single pass cylindrical mirror analyzer, a Ge-type solid-state detector, a sputter-ion gun, and other standard UHV instrumentation; a base pressure in the low 10^{-10} -Torr range was achieved.

The Cu(111) sample was cleaned by Ar⁺ sputtering and was annealed to 700 K for 5 min. The crystal was clamped onto a tantalum plate attached to a button heater which was used to raise the temperature of the sample. A chromel-alumel thermocouple clamped to the crystal was used for temperature measurements. The sample was considered clean when Auger electron spectroscopy (AES) revealed no impurities. The Rb was eva-

porated from a commercial SAES Getter source equipped with a shutter and collimator. The background pressure rise in the chamber during evaporation was less than 6×10^{-10} Torr. The determination of the coverage was done by correlating work-function measurements and dose times with our previous LEED and work-function measurements of this system.¹⁰ Our LEED study showed a (2×2) overlayer structure for one monolayer of Rb on Cu(111), which was saturation at room temperature. All Rb dosing and measurements reported here were performed at room temperature.

The BRXSW experiments were conducted by setting either the (111) or (11 $\bar{1}$) planes of the Cu(111) crystal perpendicular to the incident monochromatized x-ray beam. For the (111) reflection, the x-ray beam was incident normal to the sample surface. For the (11 $\bar{1}$) reflection, the x-rays were incident at 70.53° to the surface normal. In each case the amplitude variation and phase shift of the XSW in the Cu substrate was monitored by measuring the Cu LMM Auger electron yield at 920-eV kinetic energy as the photon energy was scanned through the back reflection Cu(111) dynamical Bragg diffraction condition around 2975 eV. The adsorbed Rb atomic position relative to the Cu lattice was determined by monitoring the Rb 2p_{3/2} photoemission peak at 1170-eV kinetic energy while performing the photon-energy scan through the Bragg rocking curve. In Fig. 1, we present a typical electron-energy distribution curve of the region containing the relevant peaks. In addition, further photon-energy scans were recorded at electron kinetic energies 10 eV above each of these peaks; these were used for background subtraction and for determining the true electron yield response. Simultaneously with the XSW signal, the reflectivity spectra were measured with two nickel grids.

III. RESULTS

In Fig. 2 we present the results of XSW measurements for the (2×2) phase of one monolayer of Rb on Cu(111) in the (111) and (11 $\bar{1}$) geometries. For each reflection

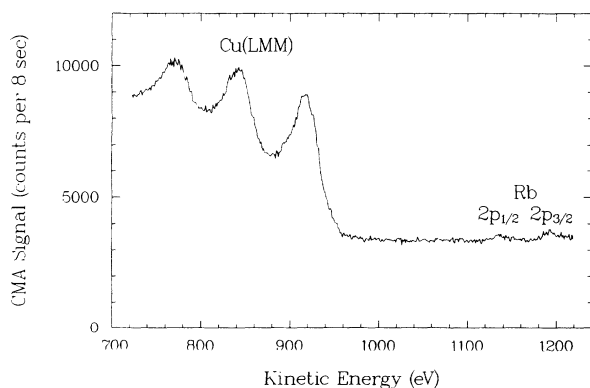


FIG. 1. Electron-energy distribution spectrum for one monolayer of Rb on Cu(111), measured with a CMA using an ~ 3000 -eV monochromatic x-ray beam at normal incidence. The Cu LMM Auger peaks and the Rb 2p_{1/2}, and 2p_{3/2} photoemission peaks are indicated.

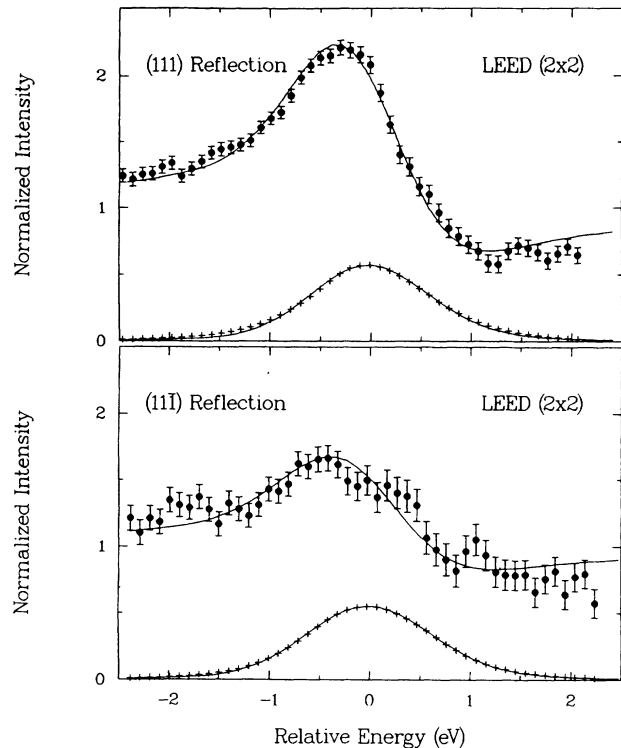


FIG. 2. Energy dependence of the Rb photoelectron standing-wave yields for both the (111) and (11 $\bar{1}$) reflection planes are shown in the upper curves for one monolayer of Rb/Cu(111). The lower curves are the measured reflectivities and the solid lines are fits using dynamic diffraction theory.

plane, the lower curve is the reflectivity and the upper one represents the appropriate Rb photoemission yield, normalized to unity away from the Bragg reflection. The solid lines are fits to the data. The reflectivity curves were fitted by convoluting the Gaussian-type instrumental resolution function with the intrinsic Darwin-Prins reflectivity curve. The same Gaussian broadening of width 0.75 eV was also used in fitting to the Rb photoelectron-yield data. The adsorbate photoelectron-yield in the standing wave field is given by

$$Y(E)/Y_{0B} = 1 + R(E) + 2\sqrt{R(E)}f \cos(v[E] - 2\pi\phi).$$

Here the reflectivity is

$$R(E) = \left| \left[\frac{E_H}{E_0} [E] \right] \right|^2,$$

where E_0 and E_H are the incident and diffracted beam electric-field amplitudes, respectively; $v[E]$ is the energy-dependent phase of E_H relative to E_0 ; Y_{0B} is the emission yield away from the Bragg reflection; and f and ϕ are the so-called coherent fraction and coherent position. They represent, respectively, the spread of positions taken on by the adsorbate atoms, and the weighted average position of the atoms relative to the diffraction planes. The coherent position takes on a value between $-\frac{1}{2}$ and $+\frac{1}{2}$, with a value of 0 corresponding to a position on the planes, and $\pm\frac{1}{2}$ corresponding to a position midway between the planes. The coherent fraction

comprises the product of a thermal Debye-Waller factor for the adsorbate, a factor determined by static disorder, and a geometrical factor which includes the effect of multiple-site adsorption relative to the reflecting planes. A value of unity for the coherent fraction means that all the Rb atoms are located at the same (coherent) position relative to the diffraction planes, while a value of less than 1 for the coherent fraction means that more than one position is occupied or there is some type of disorder in the system.

Table I lists the coherent position and coherent fraction values for the data shown in Fig. 2. The (111) reflection data for Rb yields a coherent position of 0.473 and a coherent fraction of 0.99. The high coherent fraction value (0.99) indicates that all Rb atoms lie in a single plane parallel to the Cu(111) surface, and is consistent with the single site suggested by the (2×2) LEED pattern. In the case of the $(11\bar{1})$ reflection planes, the Rb coherent position is 0.55 with a coherent fraction (0.54) lower than for the (111) case. Therefore, the degree of order of the Rb atoms is high perpendicular to the surface, but lower parallel to the surface. These data were remeasured several times and also as a function of time following a given deposition. As a function of time, the (111) coherent position and fraction and the $(11\bar{1})$ coherent position hardly varied, whereas the $(11\bar{1})$ coherent fraction varied greatly, decreasing with increasing time, probably due to the effect of contamination. The value shown in Table I was the highest observed. Given these trends and the (2×2) LEED patterns, we suggest that a single site parallel to the surface is occupied, but with an occupation index which decreases with time. We will discuss this further below.

IV. Rb-ATOM LOCATION

The combination of the (111) and $(11\bar{1})$ Rb-Cu layer spacings found in these measurements allows us to determine the specific adsorption site. In particular, taking the measured (111) layer spacing, one can calculate the anticipated $(11\bar{1})$ layer spacing for different adsorption sites, and compare these values with the experimental $(11\bar{1})$ data. Note that there is an ambiguity in all XSW layer spacings in that any periodicity of the substrate plane layer spacing [2.08 Å for Cu(111)] may be added to the measured value. For the fcc(111) surface the close-packed layers are stacked in an $ABCABC \dots$ sequence which repeats every third layer.¹⁹ This leaves three possible adsorption sites: atop, or one of the two three-fold coordinated hollow sites, "fcc" or "hcp," corresponding to sites directly above Cu atoms in the third or second substrate layer, respectively.

Figure 3 is a schematic diagram showing the possible adsorption sites relative to the (111) and $(11\bar{1})$ planes. In

TABLE I. Values of coherent position ϕ and coherent fraction f , for 1 ML Rb/Cu(111), from the data presented in Fig. 2.

Reflection planes	ϕ	f
(111)	0.473±0.005	0.99±0.03
$(11\bar{1})$	0.55±0.02	0.54±0.04

Table II we adopted a format similar to that of Ref. 5 for the system Rb/Al(111). Based on our triangulation results (presented in Table II), we obtained three possible adsorption sites: the hcp hollow site with an Rb-Cu(111) bond length of 0.99 Å, the atop site with an Rb-Cu(111) bond length of 3.07 Å, or the fcc hollow site with a bond length of 5.15 Å. The nearest-neighbor adsorbate-substrate distances in these three structures are obviously very different. By subtracting the metallic Cu radius, we obtain the effective Rb radii for all three adsorption sites (shown in the last column of Table II). As we can see clearly, the only physically reasonable solution corresponds to atop site adsorption with an effective Rb radius of 1.79 Å, which is in the range between the Rb ionic radius (1.48 Å) and the metallic radius (2.43 Å). It should be pointed out that all of the above numbers are only exact if the Cu substrate atoms occupy ideal bulk sites. If there is any deviation of the surface atoms from bulklike positions, then these values must be adjusted accordingly.

Returning to the relatively low measured coherent fraction value for the $(11\bar{1})$ planes, this indicates that the Rb overlayer is more disordered laterally than perpendicular to the surface. Similar observations have been reported by Kerkar *et al.*⁵ for Rb/Al(111) using BRXSW and Alder *et al.*⁸ for K/Cu(111), Ni(111) using I/Cu(111), Ni(111) surface-extended x-ray-adsorption fine structure (SEXAFS). In both cases, these results were attributed to a higher surface Debye-Waller factor for the alkali overlayer parallel to the surface than in the perpendicular direction, i.e., the Rb atoms vibrate relatively easier parallel to the surface than perpendicular (dynamic disorder). This might be associated with the top site adsorption geometry, due to a soft Rb-Cu wagging vibrational mode as suggested by Kerkar *et al.*⁵ The low coherent fraction parallel to the surface could also be accounted for if the overlayer exhibits a high static disorder laterally due to displacements of the adsorbate atoms from ideal top sites. This would be the result if there were a small lattice mismatch between overlayer and substrate due to the relatively large size of the alkali adatoms. Tests of the above possibilities would be a comparison of results from different alkali adsorbates, and XSW measurements as a function of temperature.

V. DISCUSSION

Clearly our XSW results prove that the Rb atoms occupy the top sites on the Cu(111) surface for $p(2 \times 2)$ Rb/Cu(111). This is consistent with other structural observations for alkalis on close-packed metal surfaces, including Cs/Cu(111) (LEED);² Cs/Ru(0001) (LEED);³ K/Ni(111) [LEED, angle-resolved photoemission fine-structure spectroscopy (ARPEFS), SEXAFS];^{4,7,8} Rb/Al(111) (XSW);⁵ K/Al(111) (LEED);⁶ K/Cu(111) (SEXAFS);⁸ and Rb/Al(111) (LEED).⁹ The reason for the stability of on-top bonding on these systems is still being examined. Theoretical calculations²⁰ and experimental measurements⁶ of K on Al(111) suggest that top sites are favored when they are accompanied by a rumpling of the first substrate layer, such that Al atoms directly beneath K atoms are relaxed slightly towards the bulk.

TABLE II. Summary of the adsorption site determination by BRXSW triangulation using the (111) and $(11\bar{1})$ reflections for one monolayer of Rb on the Cu(111) surface. The measured (111) layer spacings (shown in column 1) are used to calculate the corresponding $(11\bar{1})$ layer spacings for atop, fcc hollow, and hcp hollow sites (shown in columns 2, 3, and 4). When these are compared with the experimental $(11\bar{1})$ data (column 5), three possible solutions are found (shown underlined in columns 2, 3, and 4). In the last column is presented the effective radius of Rb atoms calculated for these different geometries. The above values assume bulklike positions for Cu substrate and surface atoms.

Experimental (111) Spacing (\AA) $d_{111}^{\text{Cu}} = 2.08$ (\AA)	Theoretical $(11\bar{1})$ spacing			Experimental $(11\bar{1})$ spacing (\AA)	$r_{\text{Rb}}^{\text{eff}}$ (\AA)
	top	fcc hollow	hcp hollow		
0.99	0.33	1.72	<u>1.03</u>		0.50 (hcp)
or 3.07 (0.99 + 2.08)	<u>1.03</u>	0.33	1.72	1.14	1.79 (top)
or 5.15 (0.99 + 4.16)	1.72	<u>1.03</u>	0.33		4.08 (fcc)

This allows for additional screening between neighboring alkali atoms, leading to a reduction in energy through reduced adsorbate-adsorbate repulsion. The rumpling of the first layer substrate has also been reported for K/Ni(111) (Ref. 4) and Rb/Al(111).⁹

Since the standing-wave method measures the adsorbate location relative to the extended bulk substrate, we cannot determine whether a rumpling occurs for the Rb/Cu(111) system using this technique. Our XSW measurements of the substrate, using the Cu LMM Auger signal, showed coherent positions that were close to ideal

for both the (111) and $(11\bar{1})$ reflections. In both cases, however, the substrate surface sensitivity was at least six bulk layers. It should also be pointed out that the results of top sites for K/Al(111) and Rb/Al(111) (Refs. 6, 9, and 20) are metastable and the final stable adsorption sites are sixfold substitutional sites. Therefore, a direct comparison of our results with this calculation might not be appropriate. Up to now, perhaps the most important fact that can be put forward is the small energy difference between the atop site and the hollow sites due to the small substrate electron-density corrugation of the close-packed (111) surfaces and the big size of the alkali atoms.²⁰ Further theoretical calculations are needed for a better understanding of these results.

We should also like to point out that the effective radius of Rb we obtained is closer to the Rb ionic radius than the metallic radius. This has also been found for all the other top site systems studied.²⁻⁹ We should repeat that possible substrate relaxation or rumpling is not taken into account in our case [which has been found to be 0.12 \AA for K/Ni(111),^{4,7} 0.10 \AA for Cs/Ru(0001),³ and 0.25 \AA for K/Al(111) (Ref. 6)]. One explanation is that the adsorbate valence charge is sufficiently distorted that an effective "radius" is an inappropriate description of the valence charge distribution of adsorbed alkali atoms. More studies are required to clarify this issue.

In summary, we have performed adsorption site measurements for the system Rb/Cu(111) using the back reflection x-ray standing-wave method. Based on our triangulation measurements on both the (111) and $(11\bar{1})$ reflection planes, we conclude that the Rb occupies the top site on Cu(111) at saturation coverage [LEED- $p(2 \times 2)$]. The effective radius for the adsorbed Rb atoms is closer to the ionic than the metallic value. Coverage and temperature dependent measurements will be reported in a future publication.

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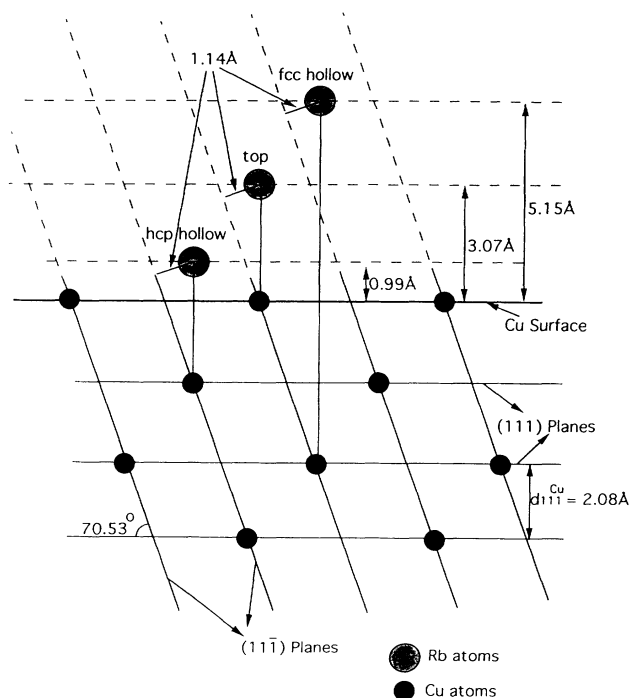


FIG. 3. A schematic illustration of Rb/Cu(111) showing the adsorption site identification by XSW triangulation for the (111) and $(11\bar{1})$ reflection planes. The horizontal dashed lines drawn above the Cu surface show the possible Rb positions based on our XSW data (see Table II).

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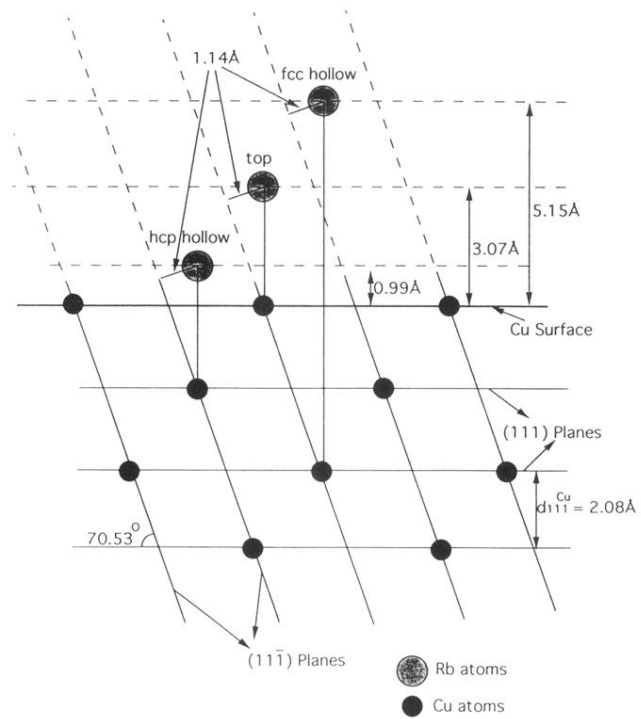


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