

Honeycomb structure of adatoms surrounding substituted atoms: Cu(111)-(2×2)-3Li

Seigi Mizuno and Hiroshi Tochiwara*

Catalysis Research Center, Hokkaido University, Kita-ku, Sapporo 060, Japan

Angelo Barbieri and Michel A. Van Hove

Materials Science Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

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We have found a type of surface structure for a (2×2) arrangement formed on Cu(111) by Li deposition at 300 K, using dynamical low-energy electron-diffraction analysis. Its unit cell contains two Li adatoms located on fcc and hcp hollow sites and one Li atom substituting for a Cu atom; the Li coverage of each component is $\frac{1}{4}$, for a total of $\frac{3}{4}$ ML. The Li adatoms form a honeycomb structure whose rings surround the substituting Li atoms.

Recently it has been recognized that adsorption of alkali-metal atoms on metal surfaces does not always imply over-layer formation,¹⁻¹⁴ in some cases alkali-metal atoms substitute for surface atoms. Furthermore, it has been suggested that with further deposition of alkali metals, ordered surface alloys can be formed at 300 K following substitutional adsorption. This has been proposed for Na on Al (Refs. 1-8) and Li on Cu.⁹⁻¹⁴ In the former system, an unusual structure was found first on Al(111): a $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure is formed by substitution of Na atoms in the top Al layer, as first determined, to our knowledge, by surface-extended x-ray-absorption fine structure (SEXAFS).¹ In addition, (2×2) and $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ structures were observed at higher coverages for Na/Al(111), and these were suggested to be surface alloys of intermixed Na-Al layers.² Composite double-layer models are proposed for the (2×2) structure.³⁻⁶ On Al(001), a $c(2\times 2)$ structure is formed by Na adsorption at room temperature, which has been proposed to be a double layer consisting of an Al layer on a Na layer on Al(001), on the basis of a SEXAFS analysis.^{7,8} For Li on Cu, anomalous low-energy electron diffraction (LEED) patterns, i.e., (2×1), (3×3), and (4×4), were observed for Li adsorption on Cu(001) at 300 K.⁹ We determined by LEED analysis that the Cu(001)-(2×1)-Li structure consists of a missing-row-type reconstruction of the top Cu layer, Li atoms being located in the missing-row sites.^{10,11} Very recently, the (3×3) structure has been determined by LEED analysis.¹² Next, Li adsorption on Cu(110) was studied with LEED observation at 300 K;¹³ (4×1) and (5×1) structures were found following a (1×2) structure proposed previously to be a missing-row structure.¹⁴ The above studies of Na on Al and Li on Cu imply that substitutional adsorption or surface alloy formation in these systems takes place independently of the crystallographic substrate surface. Therefore, it is of interest to investigate what LEED patterns and structures are observed for Li adsorption on Cu(111) at 300 K. Furthermore, it is very important to determine structures of similar systems in order to develop general surface materials concepts.

Experiments were carried out in a three-level UHV chamber equipped with standard facilities for surface science.¹⁵ Li

atoms were deposited onto Cu(111) from a SAES dispenser at 180 and 300 K. At 300 K Li adatoms grow as overlayers similar to those at 180 K up to a saturated monolayer [with coverage ~ 0.65 ML (Ref. 16)], and then a (2×2) structure is formed, which is not observed at 180 K. LEED observations and Li KVV Auger uptakes as a function of Li coverage at 180 and 300 K will be described in detail elsewhere.¹⁷ Near monolayer adsorption the observed LEED patterns are commonly observed for alkali-metal overlayers on fcc(111) surfaces at low temperatures.¹⁸⁻²¹ At 300 K a $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure, which is observed for Na on Al(111) and assigned to be a simple substituted structure,¹ is not found in the present system. With further Li deposition on the (2×2) structure, LEED patterns do not change but the background intensity increases. In the present paper we determine the Cu(111)-(2×2)-Li structure by using the automated tensor LEED scheme recently developed²² and discuss its structure. It should be noted that very few quantitative determinations of the substitutional adsorption or surface alloys have been reported so far for systems of alkali metals on metals.

Our automated tensor LEED program²² was used with six phase shifts to describe atomic scattering ($l_{\max}=5$). The real part of the inner potential was fit to experiment. The damping was represented by an imaginary part of the potential of -5.0 eV. We used 335 and 480 K for the Cu and Li Debye temperatures, respectively.²³

Thirty-six (2×2) structural models were examined for Li on Cu(111) in the present study, cf. Fig. 1. The Li coverage could not be reliably determined in the present study, because Auger uptakes of the Li KVV exhibited unusual behaviors.¹⁷ Therefore, we have investigated models with a rather wide range of possible Li coverages, from $\frac{1}{4}$ to $\frac{5}{4}$. In models 1-36, Cu and Li atoms are located on the atop or hollow site, because several studies have revealed that alkali-metal atoms can occupy either site on Cu(111).^{17,24,25} Models 1-3, 10-12, and 16-17 correspond to Li overlayers, and others involve restructuring of substrate Cu atoms. Here, we use the following convention for designating layers: "composite layers" for Li overlayers or mixed Cu-Li layers, and "substrate layers" for complete Cu(111) layers. The first composite layer contacts with the first substrate layer. The

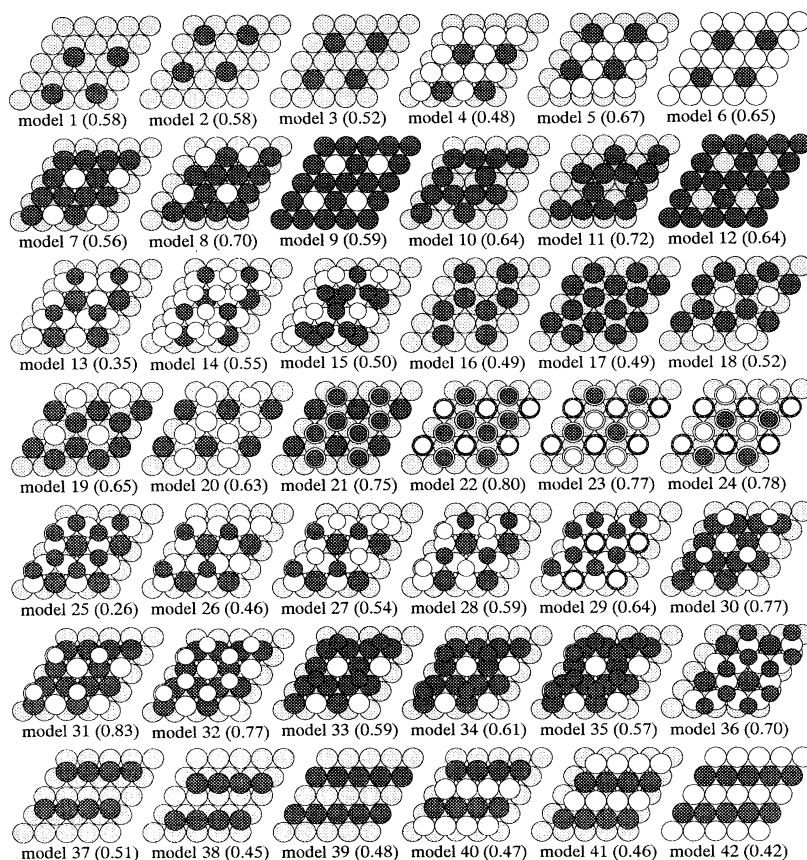


FIG. 1. Top views of examined models for the Cu(111)-(2 \times 2)-Li structure. Models 1–36 and 37–42 have (2 \times 2) and (2 \times 1) periodicities, respectively. Dark-gray spheres are Li atoms; light-gray spheres represent Cu atoms in the first substrate layer, while blank spheres are Cu atoms above that layer (first composite layer). Li and Cu atoms in the second composite layer are smaller dark-gray and blank spheres, respectively. The R_p value is given in parentheses for each model.

composite and substrate layers are numbered outwards and inwards, respectively. In models 1, 2, and 3, Li adatoms occupy the fcc hollow, hcp hollow, and atop sites on the first substrate layer shown with light-gray circles in Fig. 1, respectively. For the restructuring models, Cu atoms in the first composite layer are depicted with white circles in Fig. 1. In model 4 simple substitutions take place by Li atoms, whereas Cu atoms in the first composite layer are rearranged to occupy the hcp hollow and atop sites of the first substrate layer in models 5 and 6, respectively. Models 13–15 and 21–36 are double-layer structures. As a typical case, in the second composite layer of model 13 Li atoms (smaller dark-gray circles) are located on the fcc hollow sites of the first composite layer substituted partially by Li atoms. In model 22, Cu and Li atoms in the second composite layer occupy sites on top of Li and Cu atoms in the first composite layer. Model 23 was proposed as a possible structure for the Al(111)-(2 \times 2)-Na system,³ and models 22 and 24 are related structures consisting of diatomic molecule-type adsorbates. Model 28 was also proposed for the Al(111)-(2 \times 2).^{4,5} In addition to the 36 models above, we examined the six models 37–42 which have (2 \times 1) periodicity, cf. Fig. 1, because the (2 \times 2) LEED pattern can also be explained by three equivalent rotated domains of a (2 \times 1) structure. Models 37–39 are simple overlayers and model 40 corresponds to substitutional adsorption forming missing rows along [110]. On the other hand, Cu atoms in the first composite layer are rearranged to occupy the hcp hollow and atop sites of the first substrate layer in models 41 and 42, respectively,

forming “missing rows” similar to model 40. Li atoms are located in troughs formed by Cu atom chains.

The automated search algorithm was directed by the Pendry R_p factor, R_p , in which six inequivalent beams [(1,0), (0,1), (1,1), ($\frac{1}{2},0$), ($0,\frac{1}{2}$), and ($\frac{1}{2},\frac{1}{2}$)] were examined. Initially Li and also surface Cu atoms are put on the threefold hollow or atop sites of Cu atoms underneath in each model, and the automated search explores all their displacements that preserve the $p3m1$ and pm symmetries for models 1–36 and 37–42, respectively. Relaxations in the top two layers are allowed in these calculations. R_p values corresponding to different surface structures are given in parentheses in Fig. 1. Model 25 gives the best fit with $R_p=0.26$. All other models have much larger R_p values, except for model 13 ($R_p=0.35$). This structure is very similar to model 25, as seen in Fig. 1. The Li coverage of model 25 is 0.75. We tested models starting in sequence from 1 up. We found a much smaller R_p value of 0.26 for model 25 in comparison with models 1–24 as indicated in Fig. 1. Then, we checked structures related to 25, i.e., models 26–36, but these resulted in larger R_p values. Although other models are still possible, this search did not hint at other possibilities and was terminated.

Finally, model 25 is reoptimized with $l_{\max}=6$. The R_p value becomes 0.20. In Fig. 2, top and side views for the best-fit model are depicted. The second substrate layer (dotted circles in Fig. 2) is fixed in this optimization (in the previous optimizations the first substrate layer, light-gray circles, is fixed) and its perpendicular position is used to

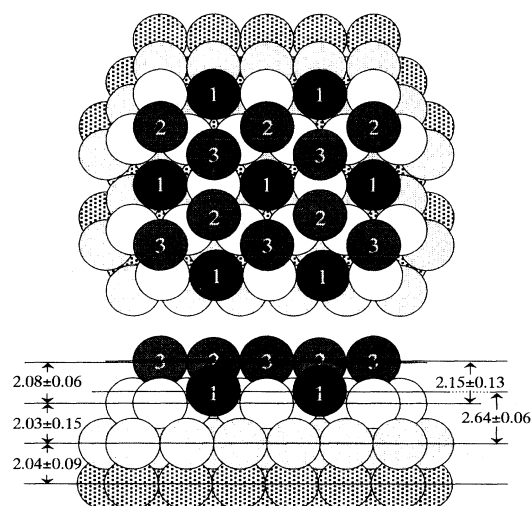


FIG. 2. Top and side views of the best-fit Cu(111)-(2 \times 2)-3Li structure (model 25 in Fig. 1). Gray levels distinguish types of atoms as in Fig. 1. The numbers identify symmetrically equivalent Li atoms. Interlayer spacings are indicated in the side view in Å.

indicate heights (perpendicular positions) of the inequivalent atoms as indicated in the side view of Fig. 2. Lateral displacements of Cu atoms in the first composite and the first substrate layers are optimized, but these are within error bars. We note that when we use a subset of beams for the optimization, the I - V curves of the other beams always agree with experiment. This strengthens our conclusion that the correct Cu(111)-(2 \times 2)-Li structure is model 25. Estimation of error bars followed Pendry's method,²⁶ using a total-energy range $\Delta E = 855$ eV. In Fig. 3, calculated I - V curves for the best-fit structure (shown in Fig. 2) are compared with experimental ones for the six beams. Agreement between theory and experiment is fairly good, and it should be emphasized that the value $R_P = 0.20$ obtained here is comparable with results for less complicated yet similar adsorption systems: 0.25 and 0.17, respectively, for the (2 \times 1) and (2 \times 2) structures formed on Cu(001) upon Li adsorption.²⁷

We emphasize some details of the determined structure (cf. Fig. 2). First, both the fcc and hcp threefold hollow sites of Cu(111) are occupied by Li atoms (numbered 2 and 3 in Fig. 2). In alkali-metal adsorption systems on fcc(111) or hcp(0001) surfaces, such occupation has not previously been reported [although Na adsorption in hcp sites on Rh(111) has been reported²⁸]. The heights of the two Li adatoms from the first composite layer (white circles of Cu atoms) are almost the same. The distance between the two Li atoms is 2.94 Å, which is slightly shorter than the bulk Li-Li distance (3.02 Å). The Li adatoms form a honeycomb lattice surrounding the substitutional sites. Second, the perpendicular position of the substituting Li atoms numbered 1 from the first substrate layer (light-gray circles) should be noted. The Li atoms may sit on the hollow sites of the first substrate layer, since the Li atoms is slightly larger than the Cu atom. It is found that the substituting Li atoms are located 2.64 Å above the first substrate layer. Li—Cu bond lengths are 2.62 and 3.02 Å for white and light-gray circles of Cu atoms, respectively. This leads to the conclusion that the Li atoms do not contact with

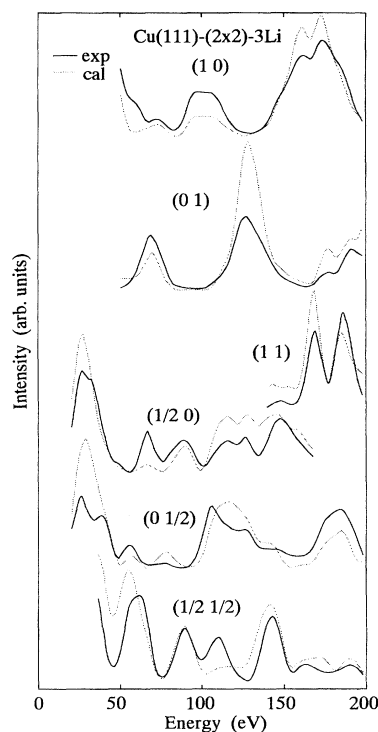


FIG. 3. Comparison between experimental (solid) and best-fit calculated (dotted) I - V curves for the Cu(111)-(2 \times 2)-3Li structure. Structural parameters for the best-fit structure are shown in Fig. 2.

the first substrate layer but sit on the sixfold coordination site, namely, on a vacant site in the first composite layer. Furthermore, we have checked the geometry in which the Li atoms are closely coplanar with Cu atoms (white circles) in the first composite layer. This results in returning to the optimized structure shown in Fig. 2 or leading to much larger R_P values.

The best-fit Cu(111)-(2 \times 2)-3Li structure [with three Li atoms per (2 \times 2) unit cell] is novel among many adstructures determined so far. A remarkable feature of this structure is six surrounding Li adatoms (hexagonal ring) around a substituted Li atom. The network of the hexagonal ring forms a honeycomb structure. The Cu(111)-(2 \times 2)-3Li structure is different from another proposed, but as yet unsolved, (2 \times 2) structure formed on Al(111) by Na adsorption at room temperature: models 23 (Ref. 3), 28 (Refs. 4 and 5), and 13 (Ref. 6) in Fig. 1.

The coverage of the Cu(111)-(2 \times 2)-3Li structure is 0.75 ML. This is reasonable, because the (2 \times 2) structure is formed after completion of the Li saturated monolayer of coverage 0.65.¹⁷ It is interesting to note that simple substituted structures having ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ or (2 \times 2) order are not produced in the present system. On the other hand, for Li on Cu(001) (Refs. 9–12) or Cu(110),^{13,14} and also for Na on Al(111),² substituted ordered structures are formed before formation of complex structures such as (3 \times 3), (4 \times 1), and (2 \times 2) or (2 $\sqrt{3}\times 2\sqrt{3}$) $R30^\circ$ at higher coverages, respectively. Understanding of the similarities and dissimilarity

ties between these systems should be addressed in the near future. Finally, it is noted that the Cu(001)-(3×3)-5Li structure, whose structure has recently been determined,¹² consists of similar components as does the Cu(111)-(2×2)-3Li structure: substituted Li atoms and Li adatoms.

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* Author to whom all correspondences should be addressed. FAX: +81-11-709-4748. Electronic address: G13787@SINET.AD.JP

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