Monte Carlo Simulation on Li Monolayer System Adsorbed on Cu(001) Surface\textsuperscript{*}

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We conducted Monte Carlo simulation for a Li system adsorbed on a Cu(001) surface at various coverage of adatoms, $\sigma > 1/2$, $\sigma = 1/2$ and $\sigma < 1/2$. We show phase diagrams of adatom arrangements, where the axes of the diagrams are the coverage $\sigma$, strength of substrate potential $\lambda$ and temperature $T$. First, we study the case in which the natural distance between adatoms is rather short, $b_{\text{nat}} < \sqrt{2}a$, where $a$ is the unit length of the substrate lattice. Then we found atoms having a "ladder structure", which fills a surface completely at $\sigma = 3/5$, as experimental results showed. At $\sigma = 1/2$, a $c(2 \times 2)$ structure is observed; the structural factor of this arrangement shows four $(\pm 1/2, \pm 1/2)$ spots in diffraction space. At $\sigma < 1/2$, we observed a complex structure including several ladder structures. The structural factor of this arrangement reproduces arced streaks connecting the four spots, as have been already observed more clearly by LEED. Second, in the case in which the natural distance between adatoms is larger, $b_{\text{nat}} \geq \sqrt{2}a$, the ladder structure does not appear at either $\sigma > 1/2$ or $\sigma < 1/2$. Streaks appear; however, they are not arced but straight lines forming a square shape.

Keywords: surface structure; adatom; monolayer; metal surface; Monte Carlo simulation; diffraction pattern; LEED

I. INTRODUCTION

Ordered structures with super-cells on simple metal monolayer atoms have been observed to adsorb on transition metal surfaces; in particular, Li on Ni(001) (See Fig. 1) [1], Mg on Cu(001) [2], and Li on Cu(001) have been observed experimentally by low-energy electron diffractions (LEED). All of them show similar tendencies in the arrangements of their adatoms.

In the experiments, several spots were observed in diffraction spaces, and several super-cell structures were proposed. The systems have been interpreted theoretically as physisorption systems such as the Frenkel-Kontorova model with mutual interactions among adatoms and the substrate potential [2, 3].

Typically, such systems have $(n\sqrt{2} \times \sqrt{2})R45^\circ$ $(n = 5, 7, 9)$ structures [1], which we call "ladder structures", at $\sigma > 1/2$, and a $c(2 \times 2)$ structure at $\sigma = 1/2$. Notice that the $c(2 \times 2)$ structure corresponds to spots at $(\pm 1/2, \pm 1/2)$, which we name M-points in a reciprocal space.

Recently, arc-shape streaks connecting the diffraction M$(\pm 1/2, \pm 1/2)$ spots have been observed by LEED in Li on Cu(001) at a low coverage, $\sigma < 1/2$ (see Fig. 2) [4].

In Section 2 of this paper, we show phase diagrams of the arrangements obtained by Monte Carlo simulation. Further, in Section 3, we reproduce the arced streaks in reciprocal space by calculating the structural factors of the adatomic arrangements.

II. MONTE CARLO SIMULATIONS AND PHASE DIAGRAMS

We conducted Monte Carlo simulation for a Li system adsorbed on a Cu(001) surface at various coverages, $\sigma > 1/2$, $\sigma = 1/2$, and $\sigma < 1/2$, with a Lenard-Jones type interaction potential having a certain natural distance between neighboring atoms and a sinusoidal substrate potential. The Hamiltonian used in this simulation is as follows:

$$H = W(r_{ij}) + V(r_j) = A \sum_{<i,j>} [(b_{\text{nat}}/r_{ij})^{1/2} - 2(b_{\text{nat}}/r_{ij})^{-6}] + E_s \sum_j |2 - \cos(\vec{g}_x \cdot \vec{r}_j) - \cos(\vec{g}_y \cdot \vec{r}_j)|,$$

where $\partial W(r_{ij})/\partial r_{ij} = 0$ at $r_{ij} = b_{\text{nat}}$; besides, $\vec{g}_x = (2\pi/a, 0)$ and $\vec{g}_y = (0, 2\pi/a)$.

The first term, $W(r_{ij}) = W(|\vec{r}_j - \vec{r}_i|)$, is the interaction energy between adatoms, and the second, $V(r_j)$, is the substrate potential, which depends on the locations of the adatoms. In addition, we define the "relative strength of the substrate potential", $\lambda$, as $\lambda \equiv E_s/A$, and a non-dimensional temperature, $T = k_B T/A$.

Hereafter, we show several atomic arrangements based on typical parameters. Then we show two types of schematic phase diagrams of the atomic arrangement of Li; one is two-dimensional, with coverage $\sigma$ as the vertical axis and the strength of the substrate potential, $\lambda$, as the horizontal axis. The other is three-dimensional, with axes of $\sigma$, $\lambda$, and temperature, $T$.

We choose two values for the natural distance between adatoms, (i) $b_{\text{nat}} = 1.39a$ and (ii) $b_{\text{nat}} = 1.52a$. We argue each case in two subsections.

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FIG. 1: \((5\sqrt{2} \times \sqrt{2})R45^\circ\) structure of Li on Ni(001) observed by LEED, Ref.1. The other systems in the text show a similar structure.

FIG. 2: Diffraction Pattern on Li on Cu(001) surface, observed by LEED, Ref.4. Arced streaks connect four M-points.

A. \(b_{\text{nat}} = 1.39a\)  
(the essential point is that \(b_{\text{nat}}\) is less than \(\sqrt{2}a\))

In this condition, adatoms fill the surface with a stable neighboring distance between adatoms of \(\sigma = 3/5\). They make a triangular lattice stably if the substrate potential is absent. If the substrate potential is finite, the atoms form a "ladder structure", in particular, a \((5\sqrt{2} \times \sqrt{2})R45^\circ\) structure, which fills a surface completely (See Fig. 3(c)).

At exactly \(\sigma = 1/2\), a \(c(2 \times 2)\) structure is observed (See Fig. 3(b)). At \(\sigma < 1/2\), we observe a complex structure with incomplete occupancy including several \((5\sqrt{2} \times \sqrt{2})R45^\circ\) structure clusters and \(c(2 \times 2)\) parts (see Fig. 3(a)). These arrangements at \(\tilde{T} = 0.5\) and \(\lambda = 2.0\) are shown in Fig. 3.

Second, we show a schematic phase diagram of \(\lambda, \sigma\)-plane at \(\tilde{T} = 0.5\) in Fig. 4(a). Here we find the interesting stability of the \(c(2 \times 2)\) phase. On the other hand, the ladder structure also has stability of re-entrance at the lower coverage region, which may cause the arc-shape streaks; we will see the streaks in the following chapter.

Finally, we show a schematic 3D phase diagram with axes \(\tilde{T}, \lambda, \sigma\) in Fig. 4(b). Here we see also a random or liquid-like phases.

Throughout the figures, we calculate for \(10 \times 10\) points on the plane of \(\sigma = 0.5\), and at least \(3 \times 3\) points on the plane of \(\tilde{T} = 0.5\).
FIG. 4: (a) Schematic 2D phase diagram of adatomic arrangements of $\lambda$, $\sigma$-plane, where $b_{nat} = 1.39a$ and $\hat{T} = 0.5$. (b) Schematic 3D phase diagram with axes $\hat{T}$, $\lambda$ and $\sigma$, where $b_{nat} \sim 1.39a$. Dark region shows sections of triangular-lattice phase, and gray regions show sections of ladder structure phase or $c(2 \times 2)$ phase.

B. $b_{nat} = 1.52a$

(The essential point is that $b_{nat}$ is equal to or greater than $\sqrt{2}a$)

The atomic arrangement consists of $c(2 \times 2)$ parts and also partially triangular parts at $\sigma > 1/2$ (See Fig. 5(c)). At $\sigma = 1/2$, it becomes a complete $c(2 \times 2)$ structure (See Fig. 5(b)). Without the substrate potential, adatoms form a triangular lattice with the natural distance, and the coverage becomes just $\sigma = 1/2$. At $\sigma < 1/2$, adatoms form clusters consisting of $c(2 \times 2)$ clusters with vacancies. Since $b_{nat} \approx 1.52a$ is nearly equal to $\sqrt{2}a$, adatoms have a "bond" with the $d = \sqrt{2}a$ of $c(2 \times 2)$ structure even at $\sigma < 1/2$ (See Fig. 3(a)).

Considering the case of $\sigma > 1/2$ again, adatoms are compressed at higher $\sigma$. Then, the interaction energy generally becomes larger than the substrate potential. In other words, the substrate potential can be suppressed effectively. Thus, adatoms may form a partial triangular lattice (See Fig. 3(c)).

Similarly to Figs. 4(a) and 4(b), we show 2D and 3D phase diagrams for $b_{nat} = 1.52a$. In Fig. 6(a), we show a schematic phase diagram of $\lambda$, $\sigma$-plane at $\hat{T} = 0.5$. Here we find that the $c(2 \times 2)$ phase can remain at lower coverage with vacancies. On the other hand, with higher coverage, pure or mixed triangular structures appear in the arrangement (see text).

Finally we show a schematic 3D phase diagram with axes $\hat{T}$, $\lambda$ and $\sigma$ in Fig. 6(b).
III. STRUCTURAL FACTORS AND ARC-SHAPE STREAKS

Here we calculate the structural factors of the arrangements obtained by the Monte Carlo simulation. We expect that some of the structural factors of the several arrangements would show arced streaks connecting the four spots, as observed experimentally in Fig. 1. We already know that the arced streak essentially originates from a second neighbor distance between adatoms (\(d = 2a\)) in a \(c(2 \times 2)\) unit in the ladder structure [4]. More specifically, the arc shape originates from a shrink and a tilt of the second neighbor pair [4] (see Fig. 7).

We must consider the same two conditions as the former section 2: namely, \(b_{\text{nat}} \approx 1.39a\) and \(b_{\text{nat}} \approx 1.52a\).

Hereafter, we argue a scenario according to Refs. 4 and 5. Since this distance is between \(d = a\) and \(d = \sqrt{2}a\), adatoms make a ladder structure. The ladder structure includes \(c(2 \times 2)\) units. A second neighbor atomic pair (the basic distance in a \(c(2 \times 2)\) unit inside a ladder structure is \(d = 2a\)), contributes to the streaks. In detail, the pair in the \(c(2 \times 2)\) unit inside the ladder structure shrinks and tilts, thereby deforming the streaks [5].

In the structural factor of an arrangement at \(\sigma < 1/2\) (specifically, at \(\lambda = 5.0\), \(\sigma = 0.45\), and \(T = 0.5\), conditions slightly different from those of Fig. 3(a), we can observe arc-shape streaks (see Fig. 8).
B. $b_{nat} = 1.52a$ (the natural distance between adatoms is slightly larger than $\sqrt{2}a$):

Since the natural distance between adatoms satisfies $b_{nat} > \sqrt{2}a$, the ladder structure does not appear either at $\sigma > 1/2$ or $\sigma < 1/2$. Streaks appear; however, they are not arced but weak straight lines forming a square shape in the reciprocal space, where we omit to show this figure.

IV. CONCLUSION

Using Monte Carlo simulation, we obtained adatomic arrangements in Li on Cu(001) under conditions of $b_{nat} = 1.39a$ and $b_{nat} = 1.52a$. In the former condition where $b_{nat}$ is relatively short, namely $b_{nat} < \sqrt{2}a$, adatoms form a ladder structure at $\sigma = 3/5$, and $c(2\times2)$ at $\sigma = 1/2$. At $\sigma < 1/2$, adatoms form a complex structure partially including the ladder structure.

Considering the condition of $\sigma = 3/5$ with $b_{nat} = 1.39a$ again, adatoms fill the surface naturally and form a $(5\sqrt{2} \times \sqrt{2})R45^\circ$ structure, which is one of ladder structures. Therefore, even at $\sigma < 1/2$, the atoms locally form a ladder structure. The second-neighbor distance of the $c(2\times2)$ unit (its normal distance is $d = 2a$) is generally shortened and tilted, especially by the existence of the zig-zag part of the ladder structure. Since the shortening and tilting of the atomic pairs occurs in many parts, greater intensity and sharpness of the arced streaks are expected.

In the second condition, $b_{nat} = 1.52a$, the distance is relatively long, $b_{nat} > \sqrt{2}a$, and the ladder structure does not exist even at $\sigma > 1/2$. Neither does it exist at $\sigma < 1/2$; thus, no arced streaks appear. Adatoms form a partial $c(2\times2)$ cluster or network, but because the natural distance between adatoms is similar to the nearest neighbor distance of the $c(2\times2)$ structure, $d = \sqrt{2}a$, only square-type streaks are produced.

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