Growth of an orientationally ordered incommensurate potassium overlayer and its order-disorder transition on the Cu(111) surface

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The evaporation of potassium onto the Cu(111) surface at 80 K results in the formation of an incommensurate orientationally ordered structure as observed by low-energy electron diffraction (LEED). The incommensurate structure appears when the potassium coverage is near 0.09, and can be characterized as a non-close-packed-hexagonal phase with an interatomic spacing continuously varying with concentration from 6.3 to 4.4 Å. As the temperature is increased, the incommensurate phase with larger K-K spacing (>5.2 Å) undergoes three transition stages as identified by LEED intensity and beam-width (full width at half maximum) measurements: (i) a better ordered hexagonal phase, (ii) a hexatic phase, and (iii) a disordered phase. The incommensurate phase with smaller K-K spacing (<5.2 Å), however, undergoes only two transition stages: (i) a better ordered hexagonal phase and (ii) a disordered phase. The incommensurate overlayer may behave as a "two-dimensional solid."

I. INTRODUCTION

Orientational growth of incommensurate monolayer films on different substrates is of interest and has been studied intensely in recent years. These kinds of structures have been observed in many experimental systems[1-4] (both physisorbed and chemisorbed). Theoretical studies of the incommensurte structure have also been successful in both prediction and explanation of observed details.[5,6] In recent years, incommensurate structures have also been observed in the systems of the alkali metals on various substrates.[7,8]

The order-disorder transition of an orientationally ordered incommensurate structure is also of interest since adatoms in that phase may realize a "two-dimensional (2D) solid" structure. The melting transition of such "2D solids" has been recently intensely studied[9-13], and the existence of a quasi-long-range-ordered melted phase ("hexatic" phase) for the melting of a triangular lattice on a smooth substrate has been noted.[10] In addition, on certain metal surfaces, alkali adatoms behave as if on a jellium substrate, as pointed out some time ago,[14,15] because of the charge transfer between the adatoms and the substrate. The two-dimensional metalization of such an overlayer might still be quite possible although some features of the monolayer film may be different from its bulk material.

In this paper we report the change of lattice parameter with coverage of a potassium overlayer on the Cu(111) surface at 80 K and the dependence of transition temperature on the lattice parameter of the overlayer.

II. EXPERIMENTAL

The experiments were carried out in an ultrahigh-vacuum (UHV) system equipped with a four grid low-energy electron-diffraction (LEED) optics. The intensities of the diffracted beams were measured from the LEED optics with a video camera interfaced to a computer. The measured intensity was integrated over a region about 10^{-4} of the first Brillouin zone. The LEED optics were also used as a retarding field analyzer for Auger-electron spectroscopy (AES). The Cu single-crystal sample with (111) surface orientation was polished (Al_2O_3 polishing paste) and then mounted onto a manipulator in the UHV system. The surface contamination and impurities were cleaned by cycles of Ar ion bombardment at 700 eV and annealing at 700 °C, until there was no indication of impurities in the AES spectrum and the LEED pattern showed sharp, high-contrast spots after annealing. The potassium was evaporated onto the sample from a thermal cell (SAES's alkali-metal dispenser) about 12 cm away. The evaporation rate was monitored by AES measurements and by the observation of the LEED pattern as well as by a quartz microbalance mounted directly under the Cu sample. The K evaporation rate was controlled at about 0.02 monolayers/min [1 monolayer (ML) $=3.7\times10^{14}$ atoms/cm^2]. The vacuum conditions of the chamber were maintained at better than 3×10^{-10} Torr during the course of experiments.

III. RESULTS AND DISCUSSIONS

The evaporation of potassium onto the Cu(111) substrate at 80 K resulted in a ring pattern at low coverage (<0.08). The coverage is defined here as the ratio of the number of the adatoms to the number of substrate atoms per unit area. A commonly assumed structure for such a ring pattern is the uniform distribution of the adatoms on the substrate with a constant adatom spacing and in hexagonal crystallines disordered with respect to the substrate.

As the coverage increased, the radius of the ring pattern increased similar to that observed for Cs on graphite.[16] When the coverage reached about 0.09, the ring intensity was modulated with the sixfold symmetry of the

substrate orientation and the ring became six discrete "spots" which were very wide in ring's annular direction. This substrate oriented phase might be like a quasi-long-range-ordered "hexatic" phase[10] with many dislocations and defects. As the coverage increased, the "spots" became sharper in the annular direction. When the coverage reached about 0.13, the LEED pattern became quite clear, however, the spots were slightly elliptical [Fig. 1(a)]. This could be a long-ranged-ordered phase with certain dislocations and defects. With further evaporation of potassium onto the substrate, the diffraction spots became brighter, the spots of the $(b_0,0)$ beam and the $(b_s-b_0,0)$ beam became closer, as shown in Fig. 2 (b_s and b_0 are the reciprocal-lattice constants of the substrate and the over-layer, respectively), and a clear commensurate (2×2) phase appeared [Fig. 2(d)]. With further increase in coverage, the $(b_s/2,0)$ beam split into two beams, the phase became incommensurate again, and finally, the beam's separation saturated with further evaporation resulting in an overall decrease of the intensity of the LEED pattern as shown in Fig. 2(f). The groups of three beams [Fig. 1(a)] [e.g., (b_0,b_0), (b_s-b_0,b_0), and (b_0,b_s-b_0)] have a similar behavior as the groups of two beams [e.g., $(b_0,0)$ and $(b_s-b_0,0)$] as the coverage was increasing.

The atomic structure of the orientationally ordered incommensurate potassium phase is proposed to be that of potassium adatoms in a hexagonal structure with the same orientation as the substrate [Fig. 1(b)]. It is still possible that the incommensurate structure is composed of some discontinuous domains, therefore, the measurement of the overlayer spots' separation (from which is extracted the potassium nearest-neighbor spacing or the overlayer lattice parameter) with coverage (Fig. 3) is illustrative in understanding more details of the adlayer structure. The data in Fig. 3 show a linear behavior of spot separation before saturating. Within the linear region the inverse square of the overlayer interatomic spacing is directly proportional to the amount of the potassium on the surface. This is in agreement with the simple model of the formation of a continuous hexagonal overlayer on the surface: the inverse square of the atomic spacing is proportional to the number of the potassium atoms per unit area in the overlayer. From Fig. 2, we can further

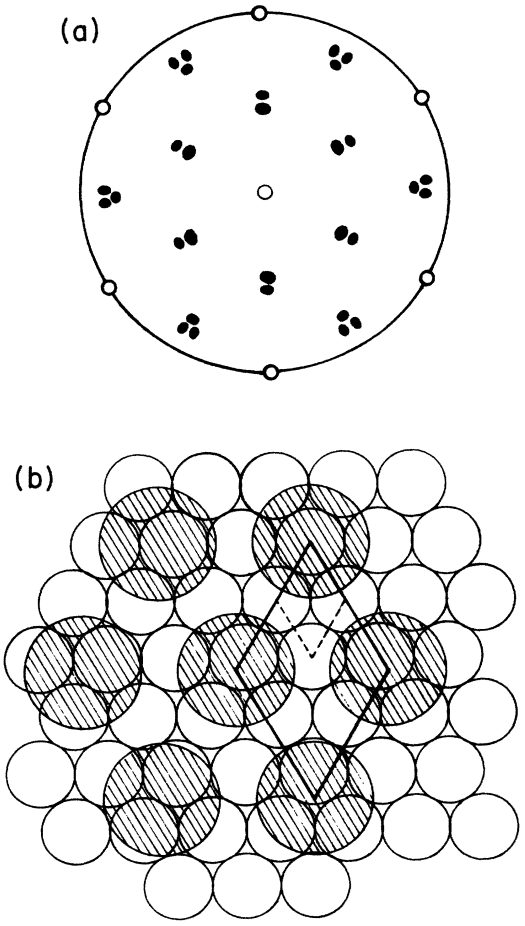

FIG. 1. (a) Schematic LEED pattern of the incommensurate phase at coverage of about 0.15 at 80 K. The extra beams are elliptical. (b) The structure of the potassium overlayer on Cu(111) of the incommensurate phase from (a). The solid and dashed lines indicate the overlayer and substrate surface unit cells, respectively.

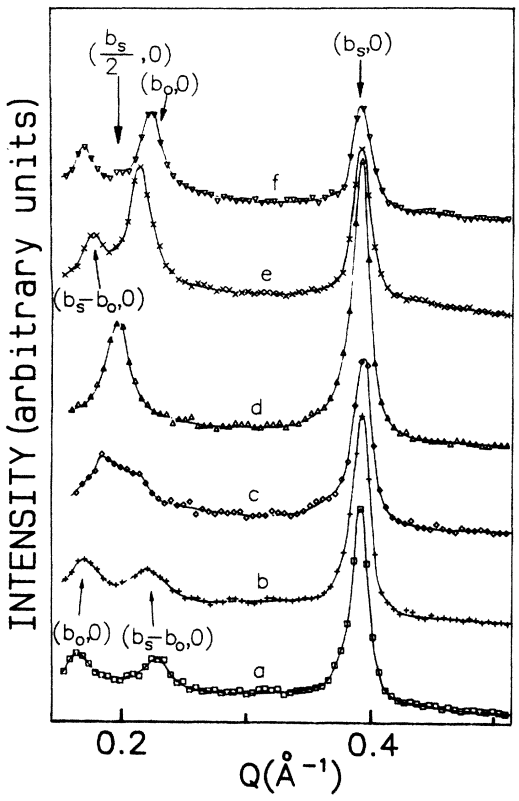

FIG. 2. The LEED beam's intensity profiles at $E=92$ eV with the increase of the potassium coverage [(a)–(f)]: (a) for a weak incommensurate phase at coverage about 0.14; (d) for a clear (2×2) phase at coverage about 0.25; (f) for a saturated incommensurate phase at coverage about 0.4. The substrate is at 80 K. b_s and b_0 are the reciprocal-lattice constants of the substrate surface and the overlayer.

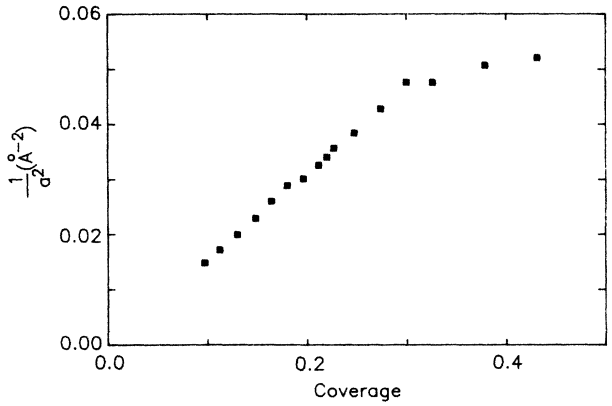

FIG. 3. Relationship between inverse square of the potassium nearest-neighbor spacing a and the potassium coverage on Cu(111) surface at 80K.

confirm that the overlayer is continuous since the FWHM's (full width at half maximum) [in the direction of $(b_s,0)$] of the extra beams do not significantly change.

From the experimental results discussed above (Figs. 1–3), it is clear that the potassium atoms form a quasi-two-dimensional solid orientationally ordered on the copper surface. The "solid" phase is first observed at 80 K for a K-K atomic spacing of about 6.3 Å which is about 35% larger than the potassium atomic diameter. The smallest observed lattice parameter for the solid potassium overlayer is 4.4 Å, slightly smaller than the potassium interatomic spacing in bulk bcc potassium. This decrease in lattice parameter is consistent with the observed lattice contraction of alkali-metal overlayers on graphite,[17] and is similar to that expected for unsupported atomic layers as pointed out earlier.[18]

In addition to the incommensurate orientationally ordered phase, a commensurate phase, $(\frac{3}{2}\sqrt{3}\times\frac{3}{2}\sqrt{3})R30°$, has been observed at room temperature for potassium coverages between 0.07 and 0.16. However, the evaporation of potassium onto the 80-K Cu(111) surface did not produce the $(\frac{3}{2}\sqrt{3}\times\frac{3}{2}\sqrt{3})R30°$ phase within that same coverage range.

The details of the incommensurate orientationally ordered phase transition have been studied through the measurement of the LEED beam intensities and the beam widths of the $(b_0,0)$ beam as a function of the K-K atomic spacing (K coverage) and temperature. Figure 4 shows the change of the LEED beam intensity and the FWHM [as measured in the $(-b_0/2,b_0)$ direction] with temperature after evaporation of potassium onto the 80-K Cu(111) surface. As temperature is increased, the incommensurate phase undergoes three phase transitions identified in the intensity curve and the FWHM curve [Fig. 4(a)]. The first transition is the incommensurate orientationally ordered phase going to a phase which is better ordered, i.e., with less defects and dislocations, identified by the decrease in the FWHM in a temperature region which is centered at T_{ca} [Fig. 4(a)]. The second one is the transition from the better ordered hexagonal phase to a hexatic phase with a significant increase in dislocations identified by the increase of the FWHM at

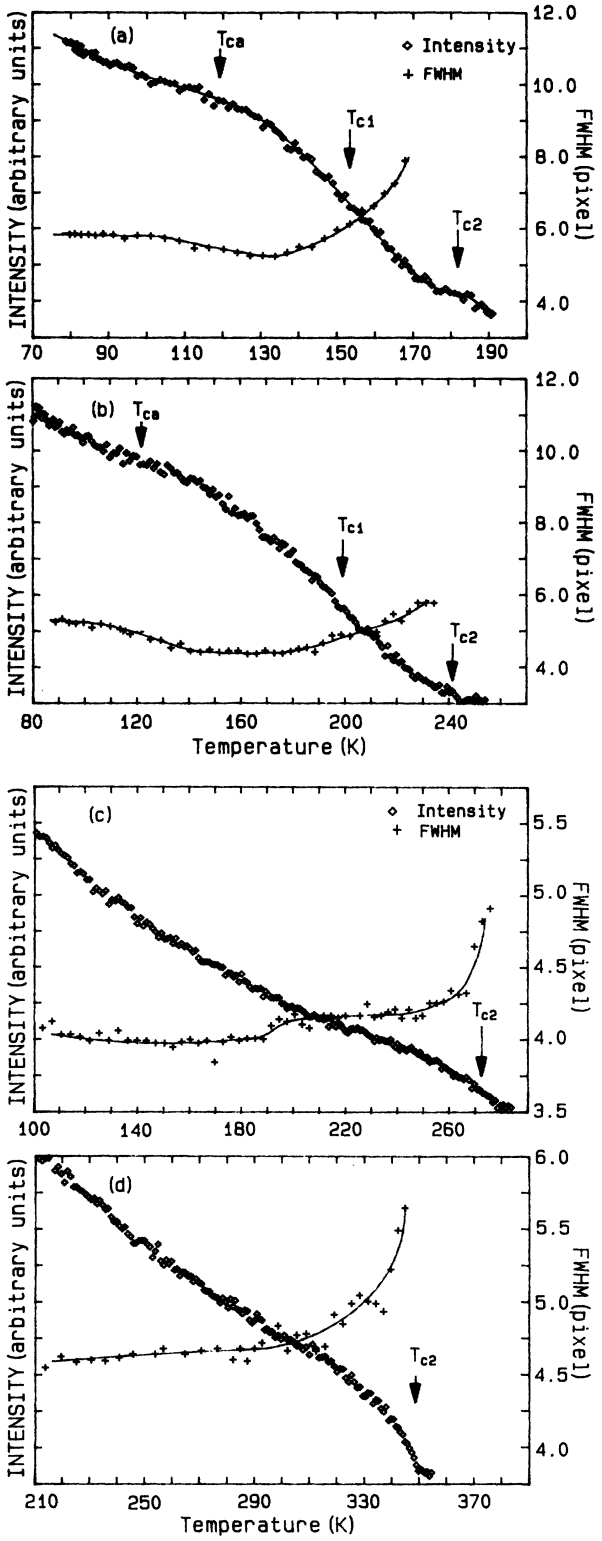

FIG. 4. Change of the LEED intensity and the beam width [FWHM is measured in $(-b_0/2,b_0)$ direction] of the $(b_0,0)$ beam as a function of temperature after evaporation of potassium onto Cu(111) surface at 80 K. The overlayer lattice parameter is (a) 5.65 Å; (b) 5.33 Å; (c) 5.17 Å; (d) 4.54 Å. One pixel is equivalent to 1.3×10^{-2} of the reciprocal-lattice parameter (b_s) in this measurement. The curves are to aid the eye in studying the data.

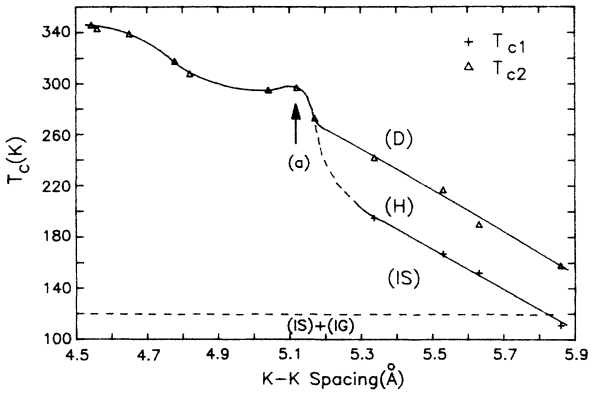

FIG. 5. Relationship between the transition temperatures as a function of the overlayer lattice parameter (K-K spacing). The dashed line at 120 K indicates T_{ca}. The K-K spacing can be converted to the coverage (Fig. 3). (*a*) indicates the value of K-K spacing for the (2×2) structure. (IS) represents the incommensurate solid phase, (IG) the immobile gas, (H) the hexatic phase, and (D) the disordered phase.

T_{c1} [Fig. 4(a)]. Transition temperature T_{c1} is defined by the inflection point of the decrease of intensity within the wide, symmetric transition region. The third one is the transition from the hexatic phase to a completely disordered phase at T_{c2}, identified with further decrease in LEED intensity and the tendency of divergence in the FWHM.

Increasing the coverage (or decreasing the lattice parameter) of the overlayer results in change in the transition features as shown in Figs. 4(b)–4(d). The transition temperatures, T_{c1} and T_{c2}, increase with coverage, and the hexatic phase region becomes less obvious [Figs. 4(b) and 4(c)]. The transition temperature T_{ca} at 120 K is believed to be independent of coverage as indicated in Figs. 4(a) and 4(b), and the transition is irreversible. The step in the FWHM curve [Fig. 4(c)] at $T=195$ K is believed to be a substrate effect and not to be confused with the transition to the hexatic phase. This step is too far away from $T_{c2}=270$ K, and the overlayer lattice parameter for this sample (5.17 Å) is so close to the value for the (2×2) structure (5.12 Å) that the substrate potential wells at the (2×2) structure sites partially lock the K atoms in and create significant defects in the overlayer resulting in the increase of the FWHM at the temperature (195 K).

Further increase of the K coverage beyond 0.25 results in only a steep transition to the disordered phase at T_{c2} and probably no hexatic phase region in the intensity curves as shown in Fig. 4(d). The transition temperature T_{c2} finally reaches 347 K (about 5 K above the bulk melting temperature of potassium) as the lattice parameter of the K overlayer saturates at the value close to the nearest-neighbor spacing in bulk potassium.

A compilation of the LEED observations for the incommensurate orientationally ordered phase is given in Fig. 5. This partial phase diagram shows the transition temperatures as a function of the lattice parameter (coverage) of the potassium overlayer. The bump in the curve of T_{c2} at the position for the (2×2) structure is due to the interaction of K atoms with the Cu(111) surface, and indicates that the substrate is not completely smooth. At temperatures below 120 K, the evaporation of potassium onto the Cu(111) surface produces an incommensurate phase with certain defects and dislocations ("incommensurate solid with immobile gas" in Fig. 5), resulting from the slow migration (freezing) of the K atoms on the Cu(111) surface at low temperature. This slow migration is probably the cause of the lack of formation of the $(\frac{3}{2}\sqrt{3}\times\frac{3}{2}\sqrt{3})R\,30°$ phase at the low temperatures.

IV. CONCLUSIONS

The measured incommensurate orientationally ordered potassium overlayer on Cu(111) surface seems to behave like a "2D solid" on a smooth substrate. The phase undergoes several transitions as a function of temperature and concentration: an ordering transition, a transition to a hexatic phase, and a disordering transition. The effect of the substrate lattice periodicity on the order-disorder transition of the K overlayer is insignificant if the overlayer lattice parameter is not near the value for the (2×2) structure.

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