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Coverage-dependent adsorption sites in the K/Ru(0001) system: a low-energy electron-diffraction analysis

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The two ordered phases p(2 × 2) at a coverage $\theta = 0.25$ and $(\sqrt{3} \times \sqrt{3})$R30° at $\theta = 0.33$ of potassium adsorbed on Ru(0001) were analyzed by use of low-energy electron-diffraction (LEED). In the $(\sqrt{3} \times \sqrt{3})$R30° phase, the K atoms occupy threefold hcp sites, while in the p(2 × 2) phase the fcc site is favoured. In both phases, the K hard-sphere radii are nearly the same and close to the covalent Pauling radius.

The preferred site for an adsorbed particle within the surface unit cell is not solely determined by the minimum energy of an isolated adparticle, but also by the effective interaction between adsorbates [1–3]. As a consequence, incommensurate phases may result, but even with commensurate structures in which all adparticles are located on identical sites the sites may alter with varying coverage. An illustrative example is represented by the Cs/Ru(0001) system, for which very recently a LEED structural analysis revealed that the on-top site was preferred for the p(2 × 2) phase at $\theta = 0.25$, while for the $(\sqrt{3} \times \sqrt{3})$R30° phase at $\theta = 0.33$ the threefold hcp site was occupied [2]. Typically the adsorption geometry for adsorbed alkali metals is governed by a repulsive dipole–dipole interaction between Cs atoms. The change in the adsites could be qualitatively rationalized in the following way: on the one hand, for the on-top site in the p(2 × 2) phase as well as for the hcp site in the $(\sqrt{3} \times \sqrt{3})$ phase, a better screening between the Cs-dipoles via the substrate can be achieved, because neighbouring Cs atoms have a substrate atom in the first Ru layer directly between them. On the other hand, the energy difference between different high symmetry sites is only marginal for a Cs atom due to its large size [4].

The occupation of different adsorption sites during the formation of a crystal layer has been reported even for a monatomic system [1]: investigations with field ion microscopy of the Ir/Ir(111) system demonstrated that single Ir adatoms favour the hcp sites, while for clusters of Ir atoms the probability of occupying the bulk-like fcc sites rises rapidly with increasing cluster size, reaching nearly 100% for clusters with seven Ir atoms. Regardless of the different nature and sign of the interaction between the adparticles when comparing with an alkali/metal system, the self-adsorption of Ir is governed by strong attractive adsorbate–adsorbate interactions as reflected by the nucleation in islands at low coverages. Besides its obvious influence on the adsorption geometry this interaction accounts for a coupling of the adsites of neighbouring adparticles. For ordered alkali/metal phases, such a correlation is likewise caused by the dipole–dipole repulsion.

The adsorption of K on close-packed hexagonal metal surfaces has been studied to some extent in the past (for the system K/Ru(0001) see [5–7]), however, structural analyses were only

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performed for a few systems using LEED [8,9] and SEXAFS [10]. The K/Ru(0001) system exhibits a strong decrease of the work function with increasing coverage [5], with a minimum at $\theta = 0.25$ coinciding with an ordered p(2 × 2) structure in the LEED pattern. With increasing coverage, an ordered $(\sqrt{3} \times \sqrt{3})$ structure appears at $\theta = 0.33$. The corresponding dipole-moment of K is significantly lower than that for the p(2 × 2) phase due to mutual depolarization of K-atoms as indicated by an increase of the work function. Consequently a change in coverage is paralleled by a modification of the electronic properties of the adparticles, which might influence also the interaction between adsorbate and substrate and therefore might be responsible for a switching of the adsite. In this Letter we report on a LEED-structure analysis of a p(2 × 2) and a $(\sqrt{3} \times \sqrt{3})$R30° phase of the system Ki/Ru(0001), which finds a change in site attributed to this effect: in the p(2 × 2) phase K resides in a threefold fcc site, while in the $(\sqrt{3} \times \sqrt{3})$R30° structure the threefold hcp site is occupied.

The experiments were performed in a UHV chamber (base pressure: 7×10^{-11} mbar). Details about the experimental setup and sample preparation can be found elsewhere [2]. Potassium was evaporated from a well outgassed dispenser source (SAES getters, Inc.). The LEED experiments were carried out at normal incidence using a 4 grid-display LEED optics at a sample temperature of 80 K.

In the LEED program [11] 9 spin-averaged phase shifts of K and Ru were used. Details about their computation can be found in ref. [2]. For the Ru layers, the phase shifts were temperature corrected using a fixed effective Debye temperature of 420 K. The Debye temperature of K was kept fixed at 160 K. The agreement between experimental and theoretical intensity data was quantified both by the R_{DE}-factor introduced by Kleinle et al. [13] and by Pendry's R-factor R_P [14]. A nonlinear least-squares optimization scheme [12] allowing a simultaneous refinement of structural parameters and the real part of the muffin tin zero was partially applied.

In order to get an overview about local minima in the R-factor surface and thus suitable starting configurations for an automatic structural refinement, in the $(\sqrt{3} \times \sqrt{3})$R30° structure the K–Ru interlayer spacing and the lateral K position along line x (see fig. 1a) was varied by a coarse-meshed grid search. A total number of 254 data points in 3 integer and 4 fractional order beams was used for comparison with experiment. The first Ru interlayer spacing was kept fixed at 2.09 Å corresponding to the value of the relaxed clean Ru(0001) surface [15]. The grid search is illustrated by a two-dimensional Pendry-R-factor plot (see fig. 1b), which shows a significant preference

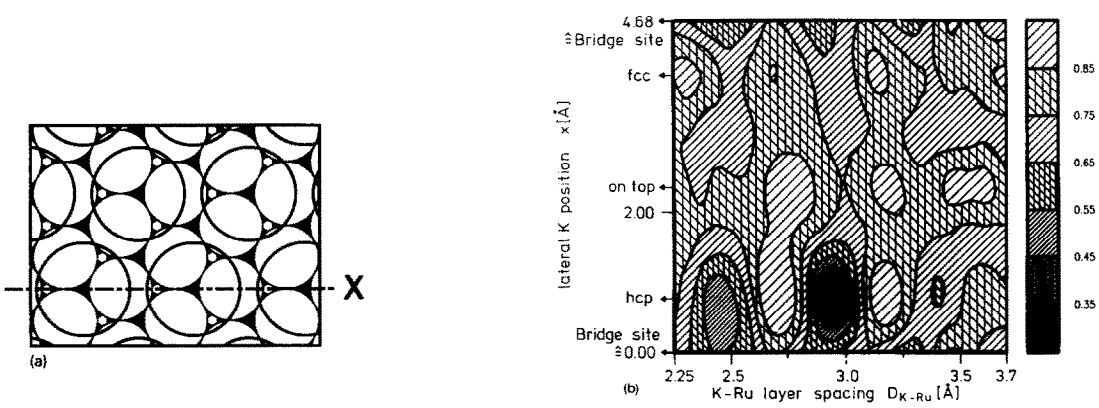

Fig. 1. (a) Structural model of K/Ru(0001)-$(\sqrt{3} \times \sqrt{3})$R30°; the lateral position of potassium was varied along line x between the points indicated by the arrows. (b) Pendry R-factor as function of the K–Ru interlayer spacing and the lateral K-position in the $(\sqrt{3} \times \sqrt{3})$R30°-phase.

Table 1
R-factors for the best fit arrangement of the respective K adsorption sites

Adsite	K/Ru(0001)-($\sqrt{3}\times\sqrt{3}$)R30°		K/Ru(0001)-p(2×2)	
	R_{DE}	R_P	R_{DE}	R_P
hcp	0.34	0.29	0.40	0.50
fcc	0.47	0.65	0.35	0.37
On top	0.54	0.69	0.57	0.63
Bridge	0.37	0.61	0.38	0.52

for the hcp adsorption site of potassium at an K–Ru interlayer spacing of 2.95 Å.

In a second stage, a simultaneous refinement of the K–Ru layer spacing and the topmost Ru-interlayer-spacing was performed by applying the least-squares optimization procedure. Four high-symmetry adsorption sites were intensively tested: the on top site, the bridge site and the two different threefold hollow sites hcp and fcc. The starting configurations were chosen corresponding to local minima found by the grid search. The hcp adsorption site remains clearly preferred (see table 1). Additional relaxations in the substrate, including the first two Ru interlayer spacings, a buckling in the second substrate layer as well as lateral variations in the first Ru layer, did not lead to further improvement of the R-factors.

The good agreement between the theoretical and experimental $I(E)$-curves for the hcp site at the optimal values of (2.94 ± 0.03) Å for the K–Ru interlayer spacing and (2.10 ± 0.05) Å and (2.14 ± 0.05) Å for the first two Ru interlayer spacings is demonstrated in fig. 2. The K–Ru interlayer spacing corresponds to a K–Ru bond length of (3.29 ± 0.05) Å and to a K hard-sphere radius of (1.98 ± 0.05) Å. The corresponding R-factors are $R_{DE} = 0.34$ and $R_P = 0.29$. The struc-

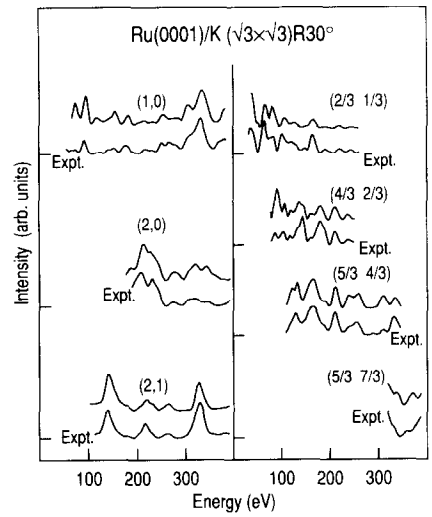

Fig. 2. Comparison of the experimental and calculated best fit $I(E)$ spectra for the $(\sqrt{3}\times\sqrt{3})$R30°-phase ($R_P = 0.29$, $R_{DE} = 0.34$).

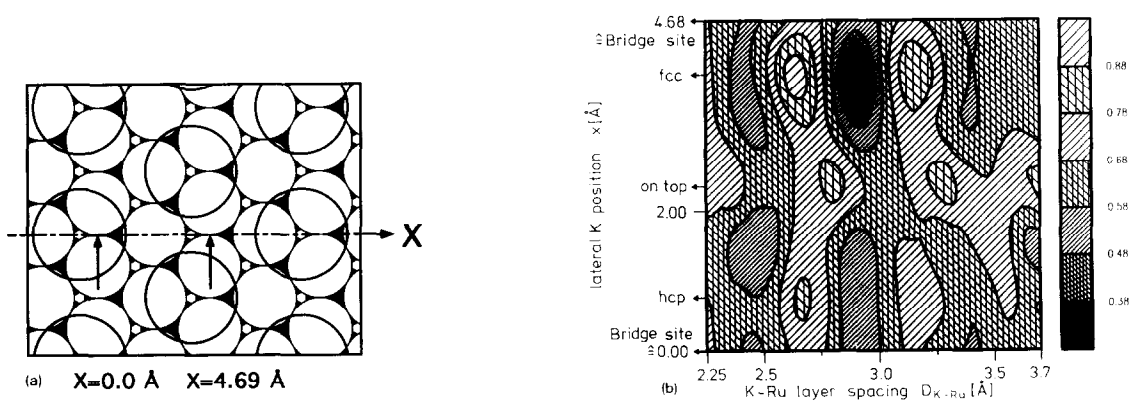

Fig. 3. (a) Structural model of K/Ru(0001)-p(2 × 2); the lateral position of potassium was varied along line x between the points indicated by the arrows. (b) Pendry R-factor as function of the K–Ru interlayer spacing and the lateral K-position in the p(2 × 2) phase.

tural results connected with the respective minima of R_{DE} and R_P coincide within 0.01 Å.

For the p(2 × 2) structure in the first stage a crude grid search was performed again by varying the K–Ru interlayer spacing and the lateral K parameter, including four high-symmetry adsorption sites as shown in fig. 3a. A total number of 298 data points in 3 integer and 5 fractional order beams was used.

In contrast to the $(\sqrt{3} \times \sqrt{3})$R30° phase, the best agreement between theory and experiment was found for the fcc site as demonstrated by the two-dimensional Pendry R-factor plot in fig. 3b. The corresponding K–Ru interlayer spacing turned out to be 2.90 Å in the R-factor minimum, which is close to the value of 2.94 Å determined for the $(\sqrt{3} \times \sqrt{3})$R30° structure.

Further refinement of the different models using the automatic optimization scheme supported the preference for the fcc site (see table 1). Apart from the K–Ru interlayer spacing, the first two substrate layer spacings and a buckling in the first Ru layer compatible with the underlying symmetry were optimized for each of the four sites. Regarding the hcp and the fcc site, an additional buckling in the second substrate layer and lateral variations in the first Ru-layer were considered, however no further improvement of the R-factors could be achieved.

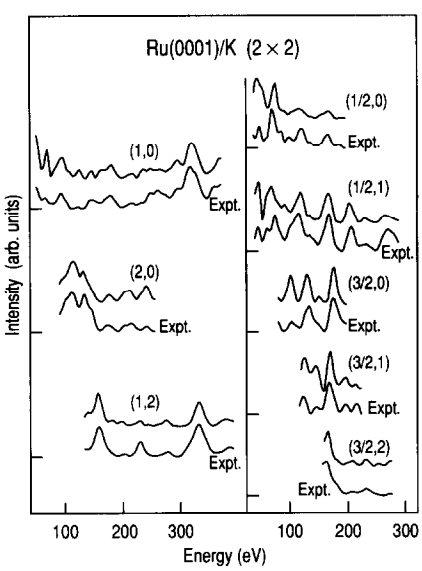

Fig. 4. Comparison of the experimental and calculated best fit $I(E)$ spectra for the p(2×2)- phase ($R_P = 0.37$, $R_{DE} = 0.35$).

In fig. 4, the experimental $I(E)$ curves for the p(2 × 2) phase are compared with the theoretical curves calculated for the optimum geometry which results in R-factors $R_{De} = 0.35$ and $R_P = 0.37$. Both R-factor minima coincide within 0.01 Å. The potassium atom resides in a fcc site. The K–Ru interlayer spacing takes the value (2.90 ± 0.03) Å, corresponding to a K–Ru bond length of (3.25 ± 0.05) Å and a K hard sphere radius of (1.94 ± 0.05) Å. The first Ru interlayer spacings values (2.12 ± 0.05) Å, and the second Ru interlayer spacing turned out to be (2.14 ± 0.05) Å, which equals the Ru bulk value.

In contrast to the Cs/Ru(0001)-p(2 × 2) system [2], potassium does not reside in the on-top site. However, the effective corrugation of the substrate potential is expected to be larger due to the smaller K radius. Thus the influence of the repulsive dipole–dipole interaction is expected to be not as dominant as for the Cs/Ru(0001) system, and screening via the substrate will play only a minor role.

Concerning the occupation of the distinguishable threefold hollow sites, the difference in the binding energy per adatom for adsorption on the hcp and the fcc site is expected to be very small. For example, total energy calculations performed for ordered structures of the K/Al(111) system [4] led to the result, that the binding energies per adatom for the two distinguishable threefold hollow sites are practically degenerate. One might therefore think of a coexistence of domains in which both fcc and hcp sites are occupied. However, an incoherent mixing of these types of domains did not lead to any improvement of the R-factors. A concentration of more than 30% fcc sites for the $(\sqrt{3} \times \sqrt{3})$R30° phase, or 30% hcp sites for the p(2 × 2) structure, produced a significant worsening of the R-factors.

At this point it is important to note that switching of large domains from one type of adsorption site to another one would represent a phase transition. In this case energy differences between the two sites only of the order of kT

would suffice to stabilize one phase over the other.

Very similar to the $(\sqrt{3} \times \sqrt{3})$R30° structure, the K hard-sphere radius of (1.94 ± 0.06) Å in the p(2 × 2) phase is close to the covalent Pauling radius of 2.03 Å [16]. This behaviour is also found in the $(\sqrt{3} \times \sqrt{3})$R30° phase of the system Cs/Ru(0001) [2] and generally is observed for alkali atoms adsorbed in highly coordinated fourfold hollow sites [17]. The K–Ru bond length in the p(2 × 2) phase of 3.25 is 0.04 Å shorter than the corresponding bondlength in the $(\sqrt{3} \times \sqrt{3})$R30° phase. In agreement with our result, theoretical calculations for the K/Al(111) system [4] indicated an increase in K–Al bond length of 0.06 Å when the K coverage changes from 0.25 (p(2 × 2) phase) to 0.33 ($(\sqrt{3} \times \sqrt{3})$R30° phase). In both cases the adsorption was assumed to be in a threefold hollow site. Qualitatively, this effect may be rationalized in terms of the decreasing effective adsorption energy with increasing coverage.

In the Cs/Ru(0001) system a more pronounced increase by 0.3 Å in the bond length was observed when changing from the p(2 × 2) to the $(\sqrt{3} \times \sqrt{3})$R30° phase. However, this enhancement is mainly caused by a switching of the Cs coordination number of the adsorption site from 1 (on top) to 3 (hcp) [2].

In summary, we could show that on Ru(0001) potassium occupies two different threefold hollow sites depending on the coverage, namely the fcc site at $\theta = 0.25$ and the hcp site at $\theta = 0.33$. The K radii of (1.94 ± 0.06) Å in the p(2 × 2) phase and (1.98 ± 0.06) Å in the $(\sqrt{3} \times \sqrt{3})$R30° structure are both close to its covalent value.

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