



The structure of K- and Cs-monolayers on Cu(001): diffraction experiments far from the Bragg point

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Abstract

The intensity analysis along the crystal truncation rods has been used to analyse in situ the adsorption behaviour and the structure of K and Cs on Cu(001) at submonolayer coverages and room temperature. Up to about 0.25 ML K atoms adsorb in hollow sites followed by formation of a quasihexagonal superstructure. In contrast, for Cs adsorption the data can be interpreted by the formation of quasihexagonal Cs islands that grow with increasing coverage. For K an effective radius of 1.6(1) Å independent of coverage is determined. For Cs we find $d_{\perp} = 2.1(1)$ Å after formation of the quasihexagonal superstructure.

1. Introduction

Many investigations have been performed in order to analyse the basic physics of alkali metal adsorption on metals. In the traditional view the alkali transfers its valence electron to the substrate to become ionic at low coverage and more covalent at adlayer completion [1]. Attention is often focused to determine the bonding length to find out the bonding character of the alkali atom. Structure investigations using LEED are limited to ordered superstructures, by the complicated multiple scattering theory and by the sensitivity of the alkali layer to the electron beam. Surface X-ray scattering is well suited for the structure analysis of the alkali adlayers.

2. Adsorption of K and Cs on Cu(001)

The measurements were performed at the beamline X16A of the NSLS in Brookhaven, USA. The Figs. 1(a) and 1(b) show as open circles the (10 0.05)_t

[2] truncation rod intensities measured versus evaporation time for K/Cu(001) and Cs/Cu(001), respectively. The moment where the evaporation sources have been switched on and off is indicated. For K we observe a decreasing intensity which passes a minimum after about 46 s followed by an increasing intensity (upper curve). Stopping the K evaporation at the minimum corresponding to about 54% of the initial intensity (lower curve shifted down for clarity) does not change the measured intensity indicating that the increase is directly related to continued K evaporation. Additionally in this case superlattice reflections were also observed.

Decrease and subsequent increase of the (10 0.05)_t intensity can be explained by initial adsorption in hollow sites and subsequent formation of a quasihexagonal superstructure [3], respectively. The total intensity I_{tot} is given by

$$I_{\text{tot}} = \left| f_{\text{Cu}} \sum_{n=-\infty}^{n=0} e^{in\psi} + \theta f_{\text{Ad}} e^{i2\pi(hx+ky+lz)} \right|^2$$

$$= \left| \frac{f_{\text{Cu}}}{1 - e^{-i\pi(h+k+l)}} + \theta f_{\text{Ad}} e^{i2\pi(hx+ky+lz)} \right|^2$$

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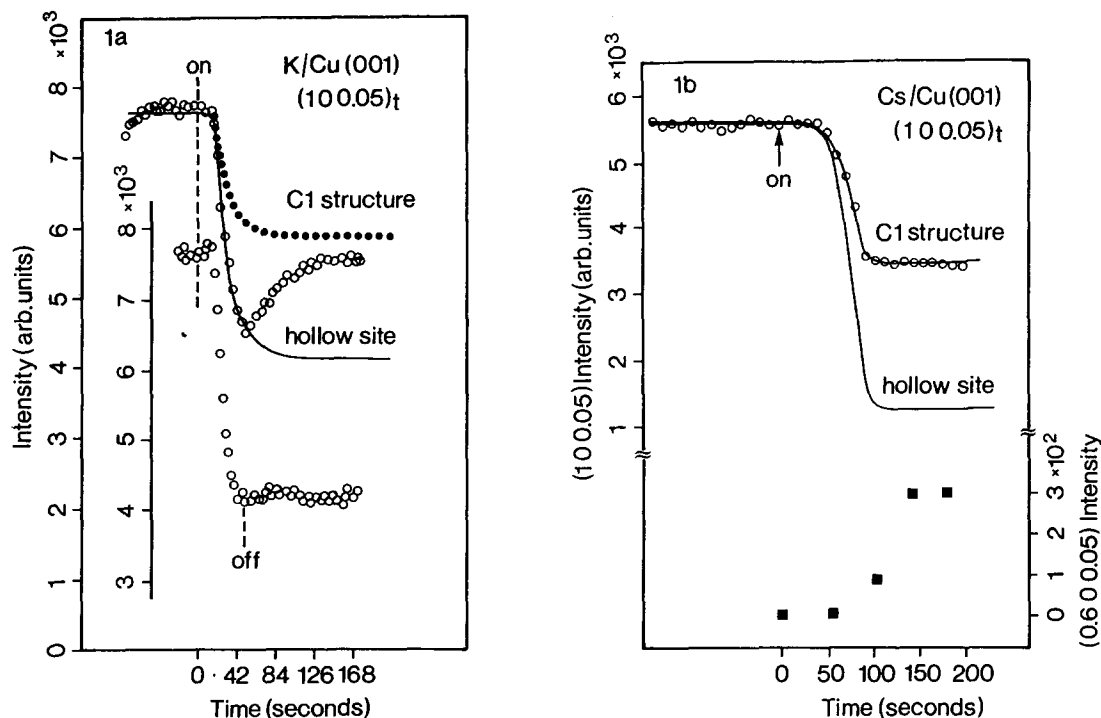


Fig. 1. (a) $(100.05)_t$ intensity (open circles) for K/Cu(001) versus evaporation time. The lower curve is shifted downwards for clarity. The solid and dotted curves represent calculations assuming pure hollow site and superstructure (C1) formation. (b) $I(100.05)$, versus time for Cs/Cu(001) (open circles). Solid lines are calculations for hollow site and superstructure formation. The filled squares indicate the intensity of the first-order superlattice reflection of the quasihexagonal overlayer $[(0.6\ 0\ 0.05)_t]$.

where ψ is the phase shift between successive layers of the substrate. The first term is the scattering amplitude of the substrate (crystal truncation rod), the second term describes the contribution of the adatom whose adsorption site within the (primitive) surface unit cell is given by the coordinates (x, y, z) . The parameters f_{Cu} and f_{Ad} are the atomic scattering factors of Cu and the adatom, respectively, θ is the relative coverage.

For the antiphase condition $(100)_t$ and hollow site adsorption $(x = 1/2, y = 1/2, z)$ we obtain $I_{\text{tot}} = |f_{\text{Cu}}/2 - f_{\text{K}}\theta|^2$ [$f_{\text{Cu}} = 23.7$, $f_{\text{K}} = 13.9$ at $(100.05)_t$]. Time dependencies $\theta(t)$ can be fitted to the measured intensities which will be discussed elsewhere. For example, the solid line assumes hollow site adsorption by $\theta(t) = \theta_{\text{max}}(1 - e^{-(t-t_0)/\tau})$, where $\theta_{\text{max}} \approx 0.30$ ML, t_0 indicates the start of the evaporation and τ is the time constant.

The subsequent increase of the $(100.05)_t$ intensity is consistent with the formation of the quasihexagonal superstructure since in this case other than hollow sites are occupied as well and the adlayer scattering is not in counterphase to the substrate as it is for hollow site adsorption. The *calculated* intensity related to the formation of the commensurate C1 structure [3] is shown by the dotted curve. The deviation from the experiment at $t > 120$ s is explained by the modulation of the evaporated incommensurate adlayer.

For Cs/Cu(001) we observe a different adsorption behaviour (Fig. 1(b)). It can be explained by the formation of quasihexagonal Cs islands which grow with increasing coverage. In Fig. 1(b) the filled squares indicate the intensity of the first-order superstructure reflection. The measured time dependency of the $(10\ 0.05)_t$ truncation rod intensity can be fitted by $\theta_{\text{C1}} \propto t^2$ suggesting

a coverage-dependent ordering of the superstructure: $\theta_{C1} \propto \theta$ and $\theta \propto t$. Preferential occupation of hollow sites at low coverage as for K is not observed. This is evident by comparison with the calculated curve in Fig. 1(b) assuming hollow site occupation by Cs ($f_{Cs} = 44.1$).

The difference between the adsorption behaviour of K and Cs can be understood in terms of the smaller size and the lower polarizability of K (4s valence electron, $r_{ion} = 1.33 \text{ \AA}$, $r_{cov} = 2.38 \text{ \AA}$) as compared to Cs (6s valence electron, $r_{ion} = 1.67 \text{ \AA}$, $r_{cov} = 2.68 \text{ \AA}$) making the K more sensitive to the substrate corrugation potential.

3. Analysis of the truncation rods

Structure information normal to the sample surface can only be achieved by the analysis along q_{\perp} , the reciprocal lattice rod normal to the sample surface. In Fig. 2 we show the ratio I_{cov}/I_{clean} of the alkali covered and the clean Cu (001) surface for Cs/Cu (001) and K/Cu (001).

From the intensity modulation we derive an adsorption height $d_{\perp} = 2.94(15) \text{ \AA}$ for Cs/Cu(001). For K/Cu(001) we find $d_{\perp} = 2.25(15) \text{ \AA}$ for K atoms adsorbed in hollow sites only (evaporator switched off at minimum (Fig. 1(a))) and $d_{\perp} = 2.10(10) \text{ \AA}$ for the quasihexagonal superstructure. In all cases the Cu interlayer distances are allowed to relax from $d_{12} = 1.788 \text{ \AA}$ and $d_{23} = 1.839 \text{ \AA}$ for the clean surface to $d_{12} = d_{23} = d_{bulk} = 1.808 \text{ \AA}$ upon alkali adsorption. Neglecting the relaxation effects leads to the dashed curves which are considerably worse fits.

Within the hard-sphere model we derive effective radii of $r_{Cs} = 2.1(1) \text{ \AA}$ for Cs and $r_K = 1.6(1) \text{ \AA}$ for K independent of coverage (0.25 ML and 0.30 ML). In previous X-ray investigations on 0.14 ML K/Cu(001) [4] we obtained $r_K = 1.5(3) \text{ \AA}$.

The comparison with the ionic and covalent radii (see above) indicates considerable charge transfer in agreement with the current view of alkali adsorption. However, in this model charge back donation at high coverage close to the completion of the adlayer ($\approx 0.30 \text{ ML}$) is expected to lead to an increase of the alkali radius which is not observed in the present investigation for K/Cu(001). This

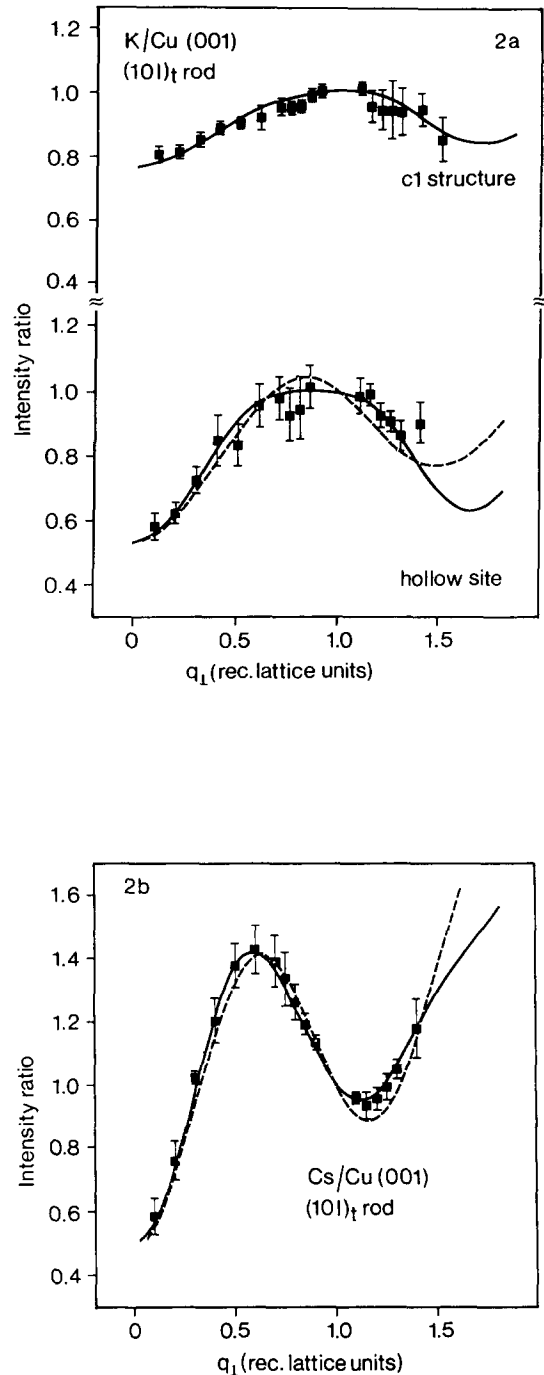


Fig. 2. (a) Ratio I_{cov}/I_{clean} along q_{\perp} for K/Cu (001) in hollow sites and for the quasihexagonal adlayer. The solid line is the best fit to the data. (b): I_{cov}/I_{clean} for Cs/Cu(001) after formation of the C1 structure. In all cases the fit shown by the dashed line neglects the substrate relaxation.

suggests that the chemisorption bond is more complex than described by the “classic” view. For example, theoretical investigations show considerable polarization of the substrate charge density due to the ionic adsorbate [5].

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