ELSEVIER

Surface Science 326 (1995) L477–L482

surface science

Surface Science Letters

Anomalous coverage behavior of the Cs–Ag distance on Cs/Ag(110)

Rolf Schuster *,[1], Peter J. Eng, Ian K. Robinson

University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Received 14 October 1994; accepted for publication 21 December 1994

Abstract

The position of Cs on the (1 × 2) missing row reconstructed Ag(110) surface was determined by X-ray diffraction for two different Cs-coverages: $\theta_{Cs} = 0.2$ and $\theta_{Cs} = 0.3$. The Cs was found to be adsorbed in incommensurate chains in the troughs of the missing row with an average adsorption height of 1.7 Å ($\theta_{Cs} = 0.2$) and 1.4 Å ($\theta_{Cs} = 0.3$) above the topmost Ag layer. The apparent contradiction to the classical picture of alkali adsorption, which expects an increase of the Cs adsorption height with coverage, might be partly resolved by introducing a fraction of commensurately adsorbed Cs at $\theta_{Cs} = 0.2$.

Keywords: Alkali metals; Low index single crystal surfaces; Metallic surfaces; Silver; Surface relaxation and reconstruction; Surface structure; X-ray scattering, diffraction, and reflection

---

A central concept in the explanation of metallic bonding in condensed matter is the mutual relationship between atomic coordination and bondlength. The expected trend of increasing bondlength with increasing coordination is nicely shown for crystalline iron: at the pressure induced transition from fcc (12-fold coordinated) to bcc (8-fold coordinated), the bondlength decreases by 2.4% [1]. This rule is embodied in the widely used formulation of "embedded atom" description of condensed matter systems, where the free energy of the system is to a first approximation determined by an "embedding term", which is solely dependent on the average charge density at the position of one atom contributed by its surrounding neighbors [2]. Maintaining this equilibrium charge density upon lowering the number of neighbors necessitates smaller distances among the remaining atoms. Surfaces, with their inherently lower coordination, should demonstrate this effect strongly, and accurate surface structure determinations are valuable in revealing its existence.

Submonolayer adsorbates on clean metal surfaces can offer a unique opportunity to test these general ideas because the coordination can be to some extent varied by adjustment of coverage: so long as the adsorbate atoms do not aggregate, the effective number of neighbors around a given atom can be varied. Not all adsorbate/surface combinations fit this description because the large majority show preference for specific binding at high-symmetry sites. Alkali metal adsorbate (neutral) atoms are relatively large

---

* Corresponding author.

[1] Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-14195 Berlin, Germany.

SSDI 0039-6028(94)00005-4

and tend to be a better choice, because the lateral corrugation of the substrate–adsorbate potential is consequently small. Compressing the alkali layer by increasing the alkali coverage then leads to a decrease of the alkali–alkali distance and subsequently to enhanced overlap of the neighbors and an effective increase of coordination of the alkali atoms. According to the above very general principle, the alkali substrate bond length should increase.

Alternative considerations of the nature of the alkali substrate bond leads to the same expectation: In the classical picture of adsorption of an isolated alkali metal atom on a metal surface the outer atomic s-electron state becomes broadened in energy and partly emptied by electron transfer to the metal. The bonding of the alkali metal towards the substrate is interpreted to be partly ionic, forming a dipole between the adatom core and its image. Recent first principle calculations have proved this model to give a reasonable insight into the physics, despite the fact that the detailed nature of the bonding between alkali metal and substrate is still under dispute [3]. Upon increasing the alkali coverage, the neighboring alkali atoms start to interact and the alkali–substrate dipoles start depolarizing each other. The "alkali ions" become increasingly neutral as the character of the bond changes from ionic at low coverages to more metallic. Therefore the bondlength between the substrate and the alkali metal is expected to increase with increasing coverage. A direct consequence of the highly polarized bonding and the resulting dipole moment are long range repulsive interactions between the alkali atoms, which at small distances, however, might be overcome by direct interactions, i.e., bond formation between the alkali atoms. In this regime the coordination argument is particularly appropriate to describe the expectations for the alkali substrate bond change.

The magnitude of the effect of coverage on the bond length should be quite large, and a number of experimental studies have been carried out to look for the trend. Whereas no change of the alkali–substrate bond length has been observed for Na/Ru(0001) [4] and K/Cu(001) [5] within the error bars, the expected trend has been established for Cs/Ag(111) [6] and Cs/Ru(0001) [7].

In this paper we present structural results for Cs/Ag(110) obtained by surface sensitive X-ray diffraction, which contradict these very general expectations: We found that the average Cs–Ag distance *decreases* with *increasing* alkali coverage. At room temperature and slightly elevated temperatures, alkali metal adsorption on the Ag(110) surface with submonolayer coverages was found to induce a (1 × 2) missing row reconstruction, where every second $[1\bar{1}0]$ Ag-row has been removed [8–11]. Equivalent behavior has also been found for the (110) surfaces of the other 3d and 4d fcc transition metals [12]. We performed a determination of the structure of the Ag(110) (1 × 2) missing row reconstruction, which included the position of the Cs for two different Cs coverages, $\theta_{Cs} = 0.2$ and $\theta_{Cs} = 0.3$; the coverage is in units of the density of the topmost layer of Ag atoms in a (1 × 1) Ag(110) surface. Surface X-ray diffraction is particularly suited to this problem [5], since deep lattice distortions are expected from the strong substrate reconstruction and the heavy Cs atoms should contribute considerably to the scattering intensities. It is also appropriate to use a reconstructed surface because the height of the reconstructed layers are a well defined reference point.

The experiments were performed at the beamline X16A at the National Synchrotron Lightsource at Brookhaven National Laboratory. The sample was mounted in a high vacuum chamber coupled to a 5-circle diffractometer. The wave length used for the experiments was 1.37 Å, corresponding to an energy of 9.08 keV. Further details on the experimental setup can be found elsewhere [13]. The Ag(110) surface was prepared by repeated Ar^+ sputtering and subsequent annealing to 650°C. Cs was evaporated from commercially available SAES getter sources. The alkali metal coverage, as well as the cleanness of the surface were monitored by Auger electron spectroscopy (AES). The (1 × 2) reconstruction was induced by depositing the required amount of Cs and subsequent annealing to 300 and 200°C for the low and high Cs coverage, which is slightly below the respective desorption temperatures of the Cs. By this procedure, well ordered domains of a (1 × 2) structure were obtained. The two Cs coverages investigated were determined from our AES measurements to be $\theta_{Cs} = 0.2 \pm 0.03$ and $\theta_{Cs} = 0.3 \pm 0.03$ using the calibration of Reiff et al. [14].

The circles and squares in Fig. 1 show the measured structure factors for the two coverages. They were obtained by integration of rocking scans of the sample with background subtraction and are normalized to the active area of the sample. For clarity only part of the data are shown. We use the LEED convention for the surface unit cell for the indication of the directions in the reciprocal lattice space, i.e., H runs along [001], K along [1$\bar{1}$0] and L is along the surface normal. The measured structure factors were fitted using a χ^2 minimization, starting from the unrelaxed missing row model of the Ag(110) surface and allowing the atoms to move according to the pmm2 symmetry of the surface unit cell, down to the fourth Ag layer (Fig. 2a). Individual Debye–Waller parameters were given for layers one and two; the rest of the Ag-atoms were considered to have the same vibrational amplitudes as bulk atoms. Because of the low overall wavevector the (0.5, 0, L) rod [15] is fairly insensitive to the distortions of deeper layers and should remain flat: This is shown by the dashed lines in Fig. 1, for which Cs has been omitted in the calculation. The fact that substantial modulation of the (0.5, 0, L) rod is observed experimentally hence directly shows that Cs has to be included in the model. The phase of these rods, with a minimum at $L = 0$, reflects an inplane antiphase shift between the main contributions to the (1 × 2) structure, namely the topmost Ag layer and the Cs. This informs us that the Cs is adsorbed in the troughs of the missing row. It was found that reasonable fits to the data could be obtained with Cs contributions only to rods with $K = 0$, which implies that Cs lies in uncorrelated, incommensurate chains along the troughs of the missing row as sketched in Fig. 2b. This is reasonable, considering also previous investigations on related systems [12]. Such a "one-dimensional" structure, disregarding the substrate corrugation, is expected to have liquid-like order along the chain directions and contributes only diffuse intensity at positions other than $K = 0$, which

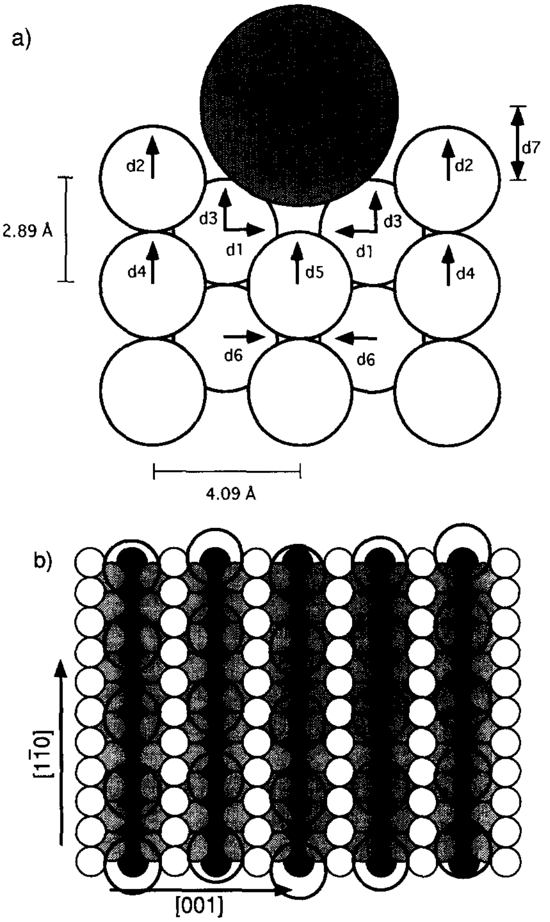

Fig. 2. (a) Side view of the (1×2) missing row reconstruction of the Ag(110) surface. (b) top view of the incommensurate chain model. The coverage is chosen to be $\theta_{Cs} = 0.20$. Note that at a coverage of $\theta_{Cs} = 0.30$ the Cs spheres would intersect. (Small circles: Ag atoms; large circles: Cs atoms; the circles have *atomic* radii.)

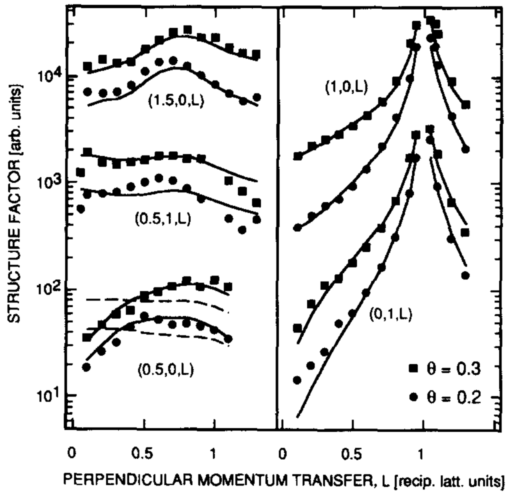

Fig. 1. Structure factors as a function of L for different H and K. The circles (squares) give the measured data for the lower (higher) Cs-coverage. The solid lines give the fitted structure factors for the full model, including Cs. The dashed lines indicate the Ag contributions to the scattered intensities at the (0.5, 0, L) rods.

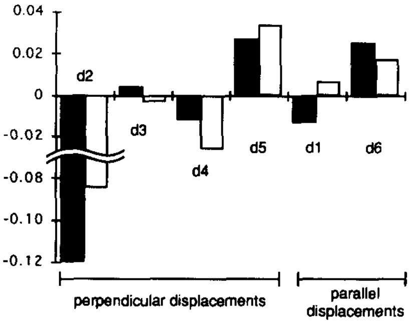

Fig. 3. Histogram of the substrate relaxations in Å for the two coverages as indicated in Fig. 2a (filled bars: $\theta_{Cs} = 0.2$; open bars: $\theta_{Cs} = 0.3$); the error bars are 0.02 Å ($d2 \pm 0.03$ Å) for the perpendicular and 0.004 Å for the parallel displacements.

can be neglected. In the *H*-direction the Cs overlayer has perfect two-fold substrate periodicity. That we need to include Cs in our model to get reasonable fits of the experimental data is a significant and new finding; other methods such as LEED [11,16] and ion scattering [10,17] applied to the structure determination of alkali-metal-induced (1 × 2) missing row reconstructions were not able to determine the alkali positions.

The solid lines in Fig. 1 show the calculated structure factors fitted to the data by applying the above model with Cs in incommensurate chains. Fig. 3 summarizes the results for the substrate relaxations. As expected from the considerable rearrangement of the Ag(110) surface into a (1 × 2) missing row structure the most important relaxation is the contraction of the first Ag-layer distance ($d2$). The values of -0.12 ± 0.03 Å and -0.08 ± 0.02 Å obtained for the lower and higher coverage, respectively, correspond to -8% and -6% of the interlayer spacing of the Ag(110) surface (1.45 Å). This is in considerable agreement with the LEED study of Barnes et al. [11], who found a contraction of the first interlayer spacing of $-11 \pm 2\%$, and with the medium-energy ion-scattering study of Frenken et al. [10], where for a potassium coverage of $\theta_K = 0.39$ a contraction of $(-9 \pm 1)\%$ was determined. The substrate relaxations and in particular their dependence on the Cs-coverage are not important to the results presented here and will be discussed in a more extended paper [18].

The Cs coverages, determined by the X-rays are $\theta_{Cs} = 0.25 \pm 0.03$ and $\theta_{Cs} = 0.29 \pm 0.03$ compared with $\theta_{Cs} = 0.2 \pm 0.03$ and $\theta_{Cs} = 0.3 \pm 0.03$ for AES. The coverage and the Debye–Waller factor of the Cs are strongly coupled parameters in the fit, which is why they are poorly determined. In our model we included isotropic Debye–Waller factors, which is certainly incorrect for the Cs adsorbed in the very anisotropic troughs [19]. This gives additional uncertainities in θ_{Cs}, not included in the error bar, so the obtained values are considered to be in agreement with the coverages determined by AES.

Just as the (0.5, 0, 0) position is sensitive to the Cs site, the position of the maximum along the (0.5, 0, L) rod reads out directly the average height of the Cs above the topmost (1 × 2) reconstructed Ag layer. We see a clear shift of this maximum towards *higher L* with *increasing* Cs coverage, which reflects directly a *decrease* of the (average) Cs height above the first Ag layer. In the fit to the data the height of the Cs above the first Ag layer drops from 1.7 ± 0.06 to 1.4 ± 0.06 Å. The corresponding Cs radii in the incommensurate chain become 2.0 to 2.3 Å for the lower Cs coverage and 2.3 to 2.6 Å for the higher coverage. This result cannot be explained in the framework of the traditional picture of alkali metal adsorption on metal surfaces, where increasing metallization should lead to an increase in bond length with increasing Cs-coverage.

This anomalous trend is the main result of the paper. Since our result contradicts the expectations of elementary theory, we now turn to consider specific mechanisms how the contradiction might be rationalized, although the *direct* evidence is rather weak. The above description of Cs in incommensurate chains is compatible with strong repulsive interactions and weak corrugation of the adsorbate–substrate potential. It therefore assumes a continuous change of the Cs–Cs spacing with coverage. We note that the absolute coverage values correspond to switching from one regime, where the average Cs–Cs distance is still larger than the atomic diameter in bulk Cs metal, to another regime, where the Cs–Cs distance is lower than the atomic diameter. More complex behavior, such as a change of the adsorption site might be expected in addition. With the fits to our incommensurate chain model mentioned above, we set all Cs atoms at one height above the Ag-substrate. However, the χ^2 value of 3.1 at $\theta_{Cs} = 0.2$ and especially the poor fit of the (0.5, 1, L)

rod indicate some remaining inadequacy in this model. We now consider the possibility of mixing different "kinds" of Cs with different adsorption sites. Indeed, upon closer inspection of Fig. 1 the badly fitted hump of the (0.5, 1, L) rod at $\theta_{Cs} = 0.2$ suggests we should include some Cs in *commensurate* positions, remembering that only Cs in such distinct adsorption sites can contribute to rods with $K \neq 0$. We considered all possible models employing a single Cs site and found that only a four-fold-coordinated hollow site with respect to the second Ag layer inside the troughs could fit the phase of the hump. Improved fits were then obtained for $\theta_{Cs} = 0.2$ by using a mixture of Cs in four-fold-coordinated hollow sites and incommensurate sites with χ^2 decreasing to 2.2. The determination of the relative heights was very poor (only the average height is strongly constrained), but the best fit was found with the incommensurate site at 1.4 Å and the four-fold-coordinated site, approximately 1 Å higher. The mixture of Cs in two different heights also improved the fit of the (0.5, 0, L) rod, i.e. the small side hump around $L = 0.5$ was now fitted correctly. For these data approximately 1/3 of the Cs was found in the commensurate positions. We note that exactly this four-fold-coordinated hollow site has been observed in recent photoelectron diffraction experiments on K/Cu(110) [20]. For the high coverage data no significant improvement of the fit was achieved with the new model.

The observed height difference of the Cs in the commensurate positions and the incommensurate chain requires different local environments of the respective Cs atoms. We therefore believe that the commensurate Cs is very unlikely to be incorporated within the incommensurate chains, and prefer to assume that two Cs-phases coexist. Recent experimental findings of island formation of alkali metal atoms on Al(111) and calculations suggest that at high alkali densities attractive forces between the alkali atoms come into play [21,22]. This could lead to a condensation into incommensurate chains. The commensurately adsorbed Cs atoms might be described as a lattice gas with a lower local Cs density, where the Cs still experiences repulsive interactions. Such a coexistence of lattice gas and condensed (one-dimensional) alkali islands has been proposed by Ref. [22].

The separation into two different phases would of course not inherently explain why the Cs in the low density commensurate phase should be adsorbed considerably higher than the incommensurate chain. However, the model provides two different Cs species with different local environments. Changing the coverage acts by changing the proportion of these two phases rather than influencing the specific bonding of the alkali atoms to the surface. The high coordination of the Cs towards the Ag surface in the commensurate four-fold-coordinated hollow site together with the very open character of the (1 × 2) missing row surface and the smeared-out electron density within the troughs [23] might provide an explanation for the large adsorption height found for this site. Nevertheless the understanding of the bonding in these fairly simple chemisorption systems clearly invites further theory and experiment.

In summary we determined the structure of the Cs/Ag(110) system for two different Cs coverages, and in particular the position of the Cs, which is adsorbed in the troughs of a (1 × 2) missing row structure. The average Cs height decreases with increasing Cs-coverage from 1.7 to 1.4 Å, which is contradictory to the classical picture of alkali metal adsorption. To account properly for the data at $\theta_{Cs} = 0.2$, we propose a model that includes a coexistence of two phases, Cs in an incommensurate chain along $[1\bar{1}0]$ and Cs in commensurate four-fold-coordinated hollow sites.

Acknowledgements

The authors gratefully acknowledge fruitful discussions with J. Neugebauer, D. Adler and H. Over. Financial support was provided by the US Department of Energy under contract DEFG02-91ER45439 and the Deutsche Forschungsgemeinschaft. NSLS is supported by DOE DEAC012-76CH00016.

References

[1] R.G.F. Wykoff, Crystal Structures, Vol. I (Wiley, New York, 1948).

[2] K.W. Jacobsen, J.K. Nørskov and M.J. Puska, Phys. Rev. B 35 (1987) 7423.

[3] M. Scheffler, C. Droste, A. Fleszar, F. Máca, G. Wachutka and G. Barzel, Physica B 172 (1991) 143;
J. Neugebauer and M. Scheffler, Phys. Rev. B 46 (1992) 16067 and references therein.

[4] T. Hertel, H. Over, H. Bludau, M. Gierer and G. Ertl, Surf. Sci. 301 (1994) 1.

[5] H.L. Meyerheim, J. Wever, V. Jahns, W. Moritz, P.J. Eng and I.K. Robinson, Surf. Sci. 304 (1994) 267.

[6] G.M. Lamble, R.S. Brooks, D.A. King and D. Norman, Phys. Rev. Lett. 61 (1988) 1112.

[7] H. Over, H. Bludau, M. Skottke-Klein, G. Ertl, W. Moritz and C.T. Campbell, Phys. Rev. B 45 (1992) 8638.

[8] B.E. Hayden, K.C. Prince, P.J. Davie, G. Paolucci and A.M. Bradshaw, Solid State Commun. 48 (1983) 325.

[9] R. Döhl-Oelze, E.M. Stuve and J.K. Sass, Solid State Commun. 57 (1986) 323.

[10] J.W.M. Frenken, R.L. Krans, J.F. van der Veen, E. Holub-Krappe and K. Horn, Phys. Rev. Lett. 59 (1987) 2307.

[11] C.J. Barnes, M. Lindroos, D.J. Holmes and D.A. King, Surf. Sci. 219 (1989) 143.

[12] R.J. Behm, in: Physics and Chemistry of Alkali Metal Adsorption, Vol. 57, Eds. H.P. Bonzel, A.M. Bradshaw and G. Ertl (Elsevier, Amsterdam, 1989) pp. 111;
R. Schuster, J.V. Barth, G. Ertl and R.J. Behm, Phys. Rev. B 44 (1991) 13689, and references therein.

[13] E. Vlieg, I.K. Robinson and K. Kern, Surf. Sci. 233 (1990) 248.

[14] S. Reiff, W. Drachsel and J.H. Block, Surf. Sci. 304 (1994) L420;
S. Reiff, PhD thesis, FU Berlin (1993).

[15] Rod or crystal truncation rod refers to the structure factors as a function of the perpendicular momentum transfer L at fixed H and K; I.K. Robinson, Phys. Rev. B 33 (1986) 3830.

[16] Z.P. Hu, B.C. Pan, W.C. Fan and A. Ignatiev, Phys. Rev. B 41 (1990) 9692.

[17] M. Copel, W.R. Graham, T. Gustafsson and S. Yalisove, Solid State Commun. 54 (1985) 695.

[18] R. Schuster, P.J. Eng and I.K. Robinson (1994), to be published.

[19] H.J. Meyerheim (1994), to be published.

[20] P. Hofmann, S. Bao, K.-M. Schindler, O. Schaff, M. Polcik, V. Fritsche, A.M. Bradshaw, R. Davis and D.P. Woodruff (1994), to be published.

[21] J.N. Andersen, E. Lundgren, R. Nyholm and M. Qvarford, Surf. Sci. 289 (1993) 307.

[22] J. Neugebauer and M. Scheffler, Phys. Rev. Lett. 71 (1993) 577.

[23] J. Tersoff and D.R. Hamann, Phys. Rev. B 31 (1985) 805.