Cs-Induced Relaxation of the Cu(110) Surface

R. Schuster* and I. K. Robinson
Department of Physics, University of Illinois, Urbana, Illinois 61801
(Received 2 August 1995)

The relaxations of a series of $(1 \times n)$ structures of the Cu(110) surface with $n = 1$, 3, 2, and 3, induced by Cs adsorption, are studied with x-ray diffraction. The distances of the topmost Cu atoms towards their underlying nearest neighbors decrease significantly with more extensive reconstruction, despite the fact that the first shell coordination of these top-layer Cu atoms does not change. Simple coordination arguments do not account for the observed trend, whereas the polarization in the surface, which is expected to increase with more extensive reconstruction, could provide an explanation.

PACS numbers: 68.35.Bs, 61.10.Nz

The systematic study of surfaces at the atomic level has opened new avenues of research into the fundamental physical principles underlying the structures of the elements. The imposition of a simple boundary on a crystal lattice significantly alters the local environment of the surface layers: This leads to the generation of new forces (of lower symmetry) and results in a structural change once the system reaches equilibrium. The study of surface structures is therefore a powerful way to gain knowledge about the workings of interatomic forces. This has important consequences when attempts are then made to predict structure from *ab initio* or semiempirical theories.

An important example of a semiempirical theory that is seeing widespread use is the effective-medium theory (EMT) [1], closely related to the embedded-atom method (EAM) [2]. The underlying assumption on this model is that the minimum of the energy of an atom in a structure is determined to first order by the charge density contributed by its surrounding neighbors. Removing surrounding atoms, i.e., changing the "coordination" of an atom, means that the remaining atoms have to come closer to provide the same optimum charge density. The change in bond length may be attributed directly to the loss of one half the atoms at a surface, i.e., to the changed coordination of those surface atoms. This effect is readily observed experimentally as a compression of the topmost surface layer in metal surfaces.

A fundamental drawback of the prescribed systematic analysis of surface structures is that any given surface has only *one* equilibrium structure to examine. Considerable advantage may be gained by the comparison of different crystallographic surfaces of the same element (for a compilation of such data see [3]), but this has limited utility because the underlying symmetries of such surfaces are different. In this work we present new results on a *homologous series* of four closely related structures, all of the same surface, Cu(110). We are able to control which structure appears with a single external variable, the coverage of an adsorbed Cs layer. We find a dramatic decrease of the nearest-neighbor (nn) distances around the top-layer atoms with the extent of the reconstruction, as the Cs coverage is increased. Because the coordination of these top-layer atoms does not change, this is in direct contradiction of the essential finding of the EMT and EAM that bond length should be related mainly to coordination.

The (1×2) missing-row reconstructions of clean Au(110) and Pt(110) are well established [4,5], while Cu(110) and Ag(110) have no reconstruction when clean. First-principles calculations can explain this difference because the specific electron distribution in the surface determines the energy. Ho and Bohnen explained the stability of the Au(110) (1×2) surface over a hypothetical (1×1) by a sensitive counterbalance of the free sp- and the localized d-electron densities in the two different geometrical arrangements [6]. They also found considerably stronger relaxations for the (1×2) missing row structure than for the (1×1), which they attributed to the stronger electrical polarization in the (1×2). This is in contrast to calculations in the EAM model, where relaxations of the Ag(110) (1×1) and the (1×2) missing row structure are essentially the same [7,8]. In order to explain the stability of these structures with EMT it is necessary to employ long-range or many-body interactions in addition to the standard coordination arguments [9]. It is clear that the extent of relaxations in such $(1 \times n)$ structures provides valuable evidence of their stabilizing principles, and that careful structural measurements will be able to guide general future improvements of the theoretical understanding of metal surfaces.

The alkali-induced missing-row structures of Cu(110) provide an excellent playground for such a comprehensive test. With increasing alkali coverage a series of well-ordered missing-row structures is formed: At $\theta_{Cs} = 0.13$ a (1×3) structure was observed by LEED [10] and STM [11]. [The coverage $\theta_{Cs} = 1$ corresponds to a density of Cs atoms equal to that of Cu in the Cu(110) (1×1) surface.] From the STM measurements a missing-row structure was determined, in which every third $[1\bar{1}0]$ row of Cu is removed. Between $0.2 \leq \theta_{Cs} \leq 0.3$ the (1×2) missing-row structure [as seen in Au(110) and Pt(110)] was found to be stable. For coverages around $\theta_{Cs} = 0.4$ the LEED investigation found a (1×3) phase [10]. All

three of these structures are confirmed in the current work, and the latter (1×3) was identified as a missing-row phase with two out of three top-layer $[1\bar{1}0]$ rows missing (see below). In the following, the (1×3) at low coverage is abbreviated by $(1 \times 3)L$, the one at high coverage by $(1 \times 3)H$.

The detailed structures of these three phases, together with the clean (1×1) surface, have been investigated by surface x-ray diffraction at the beam line X16A of the National Synchrotron Light Source at Brookhaven National Laboratory [5]. The Cu(110) surface was prepared by sputtering and annealing in UHV. Cs was evaporated from SAES getter sources. The $(1 \times 3)L$ phase was prepared by adsorption of about 0.2 ML of Cs (as estimated from the evaporation time) and subsequent desorbing of surplus Cs at 400 °C. The final coverage for the $(1 \times 3)L$ phase, as determined by our x-ray structure analysis (see below) was $\theta_{Cs} = 0.15 \pm 0.03$. For the preparation of the (1×2) phase $\theta_{Cs} \approx 0.3$ was adsorbed at 80 °C, followed by annealing at 200 °C, which reduced the Cs coverage to $\theta_{Cs} = 0.25 \pm 0.03$, as determined by x rays. The $(1 \times 3)H$ was prepared by dosing Cs at 60 °C, until the $\frac{1}{3}$ order spots of the $(1 \times 3)H$ became visible in the diffraction pattern. To preserve the structure and prevent the Cs from desorbing, this structure was cooled immediately to -100 °C. This saturated Cs layer was found to be disordered, so the Cs coverage could not be determined by x-ray diffraction (see discussion below). Because of reported multilayer formation of Cs at ≤ 50 °C the coverage in the $(1 \times 3)H$ is assumed to be about one close-packed metallic monolayer or $\theta_{Cs} \approx 0.48$ [12].

The circles in Fig. 1 show measured structure factors of the four investigated structures. They were obtained by integration of rocking scans of the sample with background subtraction and are normalized to the active area of the sample [5]. The reciprocal surface unit cell (hkl) was indexed using the LEED convention, i.e., h runs along [001], k along $[1\bar{1}0]$, and l is along the surface normal [110]. The measured structure factors were fitted using a χ^2 minimization, starting from unrelaxed surface models and allowing for horizontal and vertical displacements down to the fourth layer, while respecting the substrate symmetry. Cs was included in the model in incommensurate chains along $[1\bar{1}0]$, lying in the troughs of the reconstruction. In the data no hint for Cs adsorbed in commensurate positions towards the Cu lattice was found; due to its strong scattering factor, the Cs should show up in reciprocal space at positions with $k \neq 0$ with high sensitivity. The effective radius of the Cs was 1.98 ± 0.1 Å $\leq r_{Cs} \leq 2.22 \pm 0.1$ Å for the $(1 \times 3)L$ and 2.04 ± 0.06 Å $\leq r_{Cs} \leq 2.28 \pm 0.06$ Å for the (1×2), where the range comes from the range of possible sites in the incommensurate chain. This is reasonable if compared to the ionic Cs radius of 1.7 Å and its metallic radius of 2.7 Å. The arrows in Fig. 2 indicate the movements of the atoms from the ideal lattice positions, both

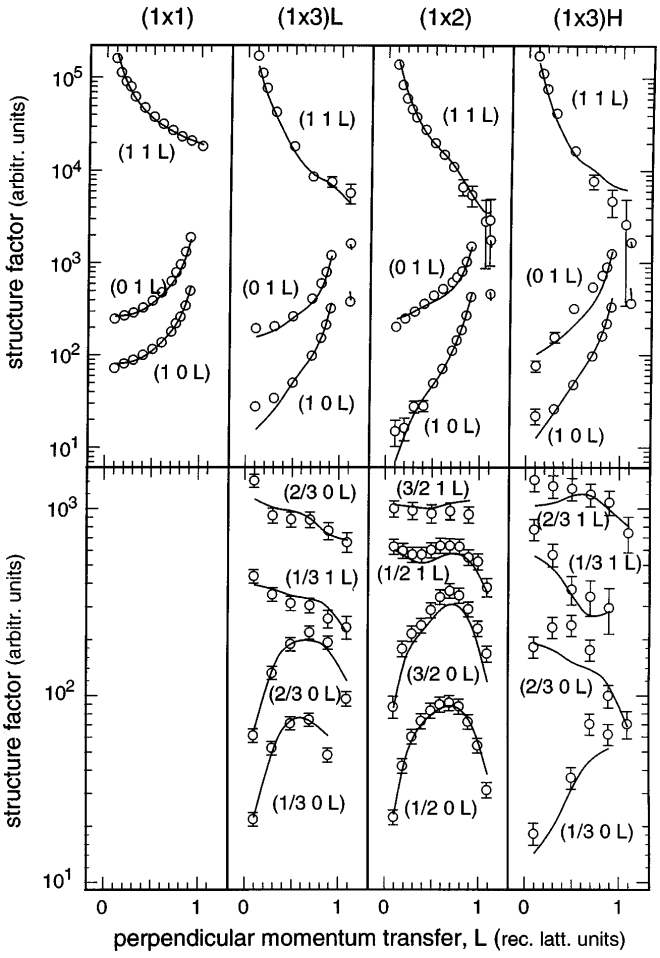

FIG. 1. Structure factors as a function of perpendicular momentum transfer L for the (1×1), $(1 \times 3)L$, (1×2), and $(1 \times 3)H$ for different in-plane momentum transfer. The circles are the measured data, whereas the solid lines show the best calculated values after χ^2 minimization of the model structures. Error bars are omitted when they are smaller than the symbols. The curves have been shifted perpendicularly for clarity.

in magnitude and direction, obtained from the complete structure determination. The calculated structure factors are depicted as solid lines in Fig. 1. A χ^2 value of 1 was obtained for the fit of the (1×1) structure, 2.8 for the $(1 \times 3)L$, 1.5 for the (1×2), and 3 for the $(1 \times 3)H$. The displacements of the (1×1) are slightly smaller than those found in a previous x-ray diffraction study [13], but within experimental error. The parameters for the (1×2) structure, especially the topmost-layer contraction, are in agreement with the LEED determination of Cs, K/Cu(110) [14], K/Ag(110) [15], and Cs/Pd(110) [16], as well as with the MEIS analysis of K/Ag(110) [17], supporting the observed stronger relaxations for the (1×2) reconstructed surface over the (1×1) structure.

The most important trend directly revealed in Fig. 2 is the large increase of the topmost-layer contraction with increasing extent of reconstruction of the surface. As

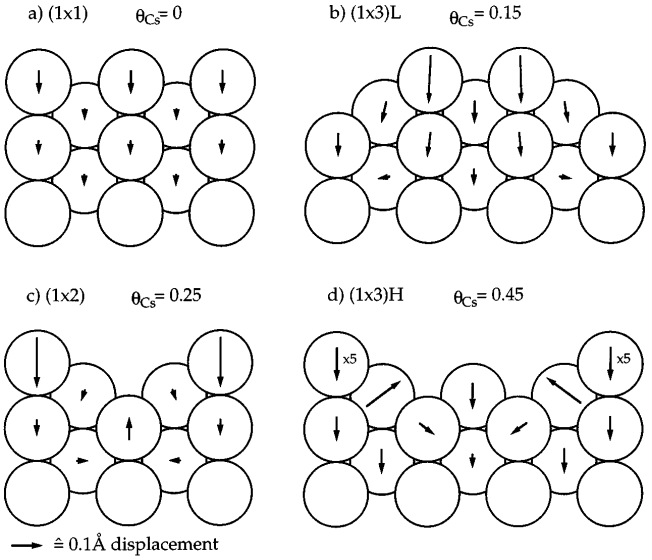

FIG. 2. Models of the four structures determined in this paper. The arrows indicate the displacements from the bulk positions, determined by the complete structure determination. The length of each arrow shaft gives the corresponding magnitude of the displacement.

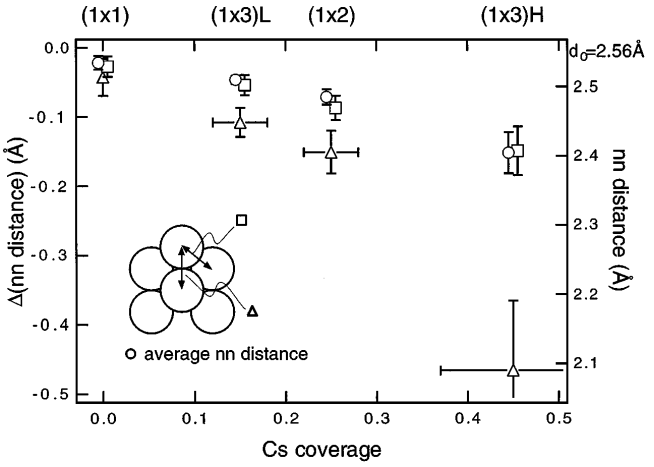

FIG. 3. nn distance as a function of the alkali coverage representing the extent of the reconstruction. Separate symbols correspond to the different neighbors and the average nn distance as sketched in the inset. For clarity, not all the coverage error bars are shown.

the local environment of the top-layer Cu atoms does not change among the different structures (the first shell coordination remains 7 Cu atoms) the strong trend is unexpected. To quantify this trend in more detail, Fig. 3 shows the measured change of the different interatomic distances around the ridge atom as a function of alkali coverage (or the extent of reconstruction). There are two independent nearest-neighbor (nn) distances that are free parameters of the model: The vertical distance to the underlying third-layer atoms and the sideways distances to the second-layer. *Both* are found to *decrease* with more extensive reconstruction. The observed displacements therefore are *not* indicative of a simple volume conserving rearrangement of the surrounding atoms in response to the reconstruction. It rather points out that the ridge atom is drawn towards *all* its neighbors with more extensive reconstruction. Coordination arguments completely fail to explain this pronounced compression of the surface with increasing Cs coverage. Since they rely almost entirely on the coordination effect, EAM-type theories would not be expected to account for the result. For example, the EAM study of the Ag(110) surface did not find differences between the relaxations in the (1×1) and (1×2) anywhere close to our observed values [7,8].

It is furthermore important to note that the direct influence of the Cs cannot explain the observed trend either. Since the (1×2) structure is stable over a relatively large coverage range ($\Delta\theta \approx 0.1$), the effect of the alkali density on the (1×2) structure can be examined in the absence of fundamental structural changes: We therefore performed experiments with the alkali coverage at the upper limit of the stability range of the (1×2) by using K instead of Cs. K, however, causes the same reconstructions as Cs at the same coverages [10]. For K/Cu(110) the relaxations (not shown) were found to be smaller than for the Cs/Cu(110) (1×2), for which the alkali coverage was smaller. This is in accordance with an earlier study of the closely related system Cs/Ag(110), where the substrate relaxations were also observed to *decrease* with *increasing* Cs coverage within the range of the (1×2) [18]. Note that this is the opposite trend to the one we are reporting among the various Cu(110) reconstructions. This direct effect of the alkali metal can be understood in terms of charge donation from the alkali metal to the surface, which increases the free sp-electron density at the metal surface, hence the pressure of the electron gas, and therefore tends to increase the Wigner-Seitz cell [19]. It should be noted that a similar trend has been observed for the adsorption of hydrogen on Cu(110) [20], where the relaxation of the surface was removed upon the hydrogen adsorption.

We now discuss the explanation of the observed trend among the four Cu(110) structures. Ho and Bohnen calculated relaxations in the (1×2) Au(110) reconstruction from first principles, which implicitly contains the polarization effects [6,21]. Their explanation of the large relaxations observed was that electrons spill out sideways from the ridge atoms towards the troughs of the missing row. This results in a dipolelike charge distribution with positive charge on the vacuum side of the ridge atom and negative charge at the bottom of the trough. The resulting force on the ion cores leads to the strong surface compression.

The above dipole argument is directly applicable to the whole series of reconstructions investigated here: As

the reconstruction becomes more extensive, the amount of negative charge redistributed from the ridges into the troughs will increase. In analogy to the Smoluchowski effect, which relates the work, function to the surface roughness [22], the dipole, which affects these ridge atoms, will increase with more massive reconstruction. The inward-directed electrostatic force on the ion cores of the ridge atoms increases therefore with more massive reconstruction. Assuming that the electrostatic force is opposed by the ion-core repulsions of each of the nearest neighbors (which do not change), this increase in the force should result directly in shorter interatomic distances. Indeed a crude estimation of the charge, needed to achieve an electrostatic displacement of atoms of proper magnitude, results in a few hundredths of an elementary charge per surface unit cell [23]. Such charge redistributions can easily be obtained at a metal surface [19]. The above arguments are analogous to the explanation of the relief of the surface relaxation in the H/Cu(110) system [20], where the reduction of the charge corrugation by the adsorbed hydrogen is thought to decrease the surface dipole and hence the relaxation.

Our experiments show a dramatic increase of the compression in the topmost Cu layer among a homologous series of structures with increasing extent of the reconstruction. This trend can be rationalized as being due to increasing electrostatic polarization across the series. Theories in which the surface energy is a function of the local geometry of the surface atoms without regarding the imbalance of the electron redistribution will therefore fail to explain these results.

The authors gratefully acknowledge fruitful discussions with J. Adams, W. Xu, M. Scheffler, and G. Vielsack. The work was supported by the U.S. Department of Energy through Grant No. DEFG02-91ER45439 and the Deutsche Forschungsgemeinschaft. NSLS is supported by DOE Grant No. DEAC012-76CH00016.

*Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany.

[1] K. W. Jacobsen, J. K. Nørskov, and M. J. Puska, Phys. Rev. B **35**, 7423 (1987).
[2] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[3] F. Jona and P. M. Marcus, in *The Structure of Surfaces II*, edited by M. A. v. Hove and S. Y. Tong (Springer, Berlin, 1988), p. 90.
[4] W. Moritz and D. Wolf, Surf. Sci. **88**, L29 (1979).
[5] E. Vlieg, I. K. Robinson, and K. Kern, Surf. Sci. **233**, 248 (1990).
[6] K. M. Ho and K. P. Bohnen, Phys. Rev. Lett. **59**, 1833 (1987).
[7] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).
[8] S. M. Foiles, Surf. Sci. Lett. **191**, L779 (1987).
[9] H. Häkkinen, J. Merikoski, and M. Manninen, J. Phys. Condens. Matter **3**, 2755 (1991).
[10] W. C. Fan and A. Ignatiev, Phys. Rev. B **38**, 366 (1988).
[11] R. Schuster, J. V. Barth, R. J. Behm, and G. Ertl, Phys. Rev. Lett. **69**, 2547 (1992).
[12] W. D. Clendening, J. A. Rodriguez, J. M. Campbell, and C. T. Campbell, Surf. Sci. **216**, 429 (1989).
[13] G. Helgesen, D. Gibbs, A. P. Baddorf, D. M. Zehner, and S. G. J. Mochrie, Phys. Rev. B **48**, 15 320 (1993).
[14] Z. P. Hu, B. C. Pan, W. C. Fan, and A. Ignatiev, Phys. Rev. B **41**, 9692 (1990).
[15] C. J. Barnes, M. Lindroos, D. J. Holmes, and D. A. King, Surf. Sci. **219**, 143 (1989).
[16] C. J. Barnes, M. Lindroos, and D. A. King, Surf. Sci. **201**, 108 (1988).
[17] J. W. M. Frenken, R. L. Krans, J. F. v. d. Veen, E. Holub-Krappe, and K. Horn, Phys. Rev. Lett. **59**, 2307 (1987).
[18] R. Schuster, P. J. Eng, and I. K. Robinson, Surf. Sci. Lett. **326**, L477 (1995).
[19] C. L. Fu and K. M. Ho, Phys. Rev. Lett. **63**, 1617 (1989).
[20] A. P. Baddorf, I. Lyo, E. W. Plummer, and H. L. Davis, J. Vac. Sci. Technol. A **5**, 782 (1987).
[21] K. M. Ho and K. P. Bohnen, Europhys. Lett. **4**, 345 (1987).
[22] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).
[23] If we assume that the force F, which gives rise to a change of $\kappa \approx 0.1$ Å in the nn distance $d \approx 2.5$ Å arises from the macroscopic elastic modulus c_{11}, then $F = c_{11}\kappa A/d$. A is approximately the surface unit cell area $\approx d^2$ and c_{11} is 1.7×10^{11} N/m^2 for copper [D. R. Linde, *CRC Handbook of Chemistry and Physics* (CRC Press, Boca Raton, 1994)]. F opposes the electrostatic force of the positive charge q on the vacuum side of the ion core, which is approximately $qe/(4\pi\varepsilon_0 d^2)$. This gives $q \approx 0.1e$/surface unit cell. Considering the above values for d as rather upper limits and that the corresponding negative charge has been neglected, charges of a few hundredths of an elementary charge have to be redistributed.