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Potassium- and sodium-induced phonons on the reconstructed and unreconstructed copper (110) surface studied by high-resolution electron-energy-loss spectroscopy

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The K- and Na-induced dipole-active vibrational modes on Cu(110) have been measured as a function of coverage at 90 and 300 K. On the reconstructed surface, in addition to the K- (Na-) substrate stretching mode, a dipole-active loss is found at 10 meV (11.5 meV). The observation of this mode even at coverages as low as $\Theta \cong 0.02$ points to local reconstruction at the lowest alkali-metal coverages. The sequence of reconstructions does not change appreciably the Na—Cu stretching frequency.

Alkali metals are known to induce "missing-row" (1×3) and (1×2) reconstructions of the (110) surfaces of Cu, Ag, Pd, and Ni at room temperature (RT).[1-4] The corresponding low-energy electron-diffraction (LEED) spots are clearly visible above a critical coverage, which for K/Cu is about 0.08.[2] However, work-function measurements[5] and LEED studies[2] suggest that local reconstruction may occur also at much lower coverages where no long-range order is present yet. Since vibrational spectra of adatoms are sensitive to the adsorption geometry, the high-resolution electron-energy-loss spectroscopy (HREELS) technique can be used to investigate the locally induced surface reconstruction.

In this Rapid Communication we report on a high-resolution EELS study of the zero-momentum dipole-active surface vibrational modes of the reconstructed and unreconstructed Cu(110) surface measured as a function of potassium or sodium coverage. On the unreconstructed surface we find a single energy-loss feature (alkali-metal–Cu stretching mode), the frequency of which does not depend on coverage. Upon reconstruction [both (1×3) and (1×2)] an additional energy-loss feature appears at about 10–11.5 meV. The latter persists down to the lowest coverage we studied, i.e., $\Theta_K \cong 0.02$, pointing to the presence of local alkali-metal-induced reconstruction even for vanishing Θ.

The Cu(110) crystal was cleaned by repeated cycles of Ar^+ bombardment and annealing, with surface order and cleanliness checked by LEED and Auger spectroscopy using a four-grid LEED system. Cleaning, alkali-metal deposition, and sample characterization were carried out in a separate chamber. K and Na were evaporated onto the surface from an SAES dispenser source at a rate of about 10^{-3}–10^{-2} monolayer/s, the pressure during evaporation was never higher than 3×10^{-10} mbar and dropped to 1×10^{-10} mbar after turning off the source. The HREEL spectra were taken in the specular direction (incidence angle 60°) with a standard ELS 22 spectrometer, operated at a working pressure of 4×10^{-11} mbar with an energy resolution of 4-6 meV and primary energies of 2.2 and 1.7 eV. The samples were biased to compensate for work-function changes.

The HREEL spectra were taken within 30 min from the alkali-metal deposition and showed no trace of contaminants (CO, H, O). Longer exposure to residual gases gave rise to changes in the intensities of the peaks (especially at high alkali-metal coverages), but did not affect their energies. At the same time contaminant peaks appeared in the energy-loss spectra.

The coverage Θ was monitored from the K- (Na-) Cu Auger peak-height ratio R. The proportionality constant between R and Θ was calculated by using the assumption that the first change in slope in the R-versus-evaporation-time curve occurs at the completion of the first layer, which corresponds to $\Theta \cong 0.6$ ($\Theta \cong 0.8$) for K (Na).

Figure 1 shows some typical HREELS spectra of the clean and alkali-metal-covered Cu(110) surface. The

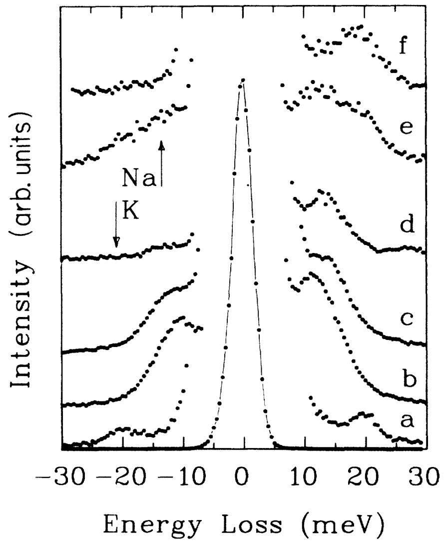

FIG. 1. HREELS spectra of the clean and alkali-metal-covered Cu(110) surface. The spectra are normalized to the elastic peak intensity. The scaling factor for each spectrum is indicated in parenthesis. (a) clean surface, RT (×200); (b) $\Theta_K = 0.13$, RT (×20); (c) $\Theta_K = 0.45$, RT (×20); (d) $\Theta_K = 0.16$, $T = 90$ K (×20); (e) $\Theta_{Na} = 0.6$, RT (×20); (f) $\Theta_{Na} = 0.13$, $T = 90$ K (×20).

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spectrum of the clean substrate (curve *a*) is characterized by a surface phonon resonance at 20 meV.[6] After dosing with K at 90 K, a strong and broad peak is observed at about 14 meV for $\Theta \leq 0.4$ (curve *d*). The energy and the intensity of this loss are plotted in Fig. 2(a) as a function of coverage. The intensity (normalized to that of the elastic peak) increases roughly linearly up to $\Theta \cong 0.1$ and vanishes for $\Theta \cong 0.4$, while the energy remains constant within 1 meV for all coverages.

Similar results were also obtained for the Θ dependence of the K- (Na-) induced losses on Cu(111) and Cu(100), both at 90 and 300 K. There the energy of the loss is about 12 meV (18 meV).[7]

In order to confirm the attribution of the observed loss to the K—Cu stretching mode, we also studied Na adsorption on Cu(110). The unreconstructed surface at 90 K is characterized by a single peak at 18 meV (see Fig. 1, curve *f*). The ratio of the vibrational frequencies of the single dipole-active losses induced by K and Na on unreconstructed surfaces is very close to the square root of the ratio between the alkali-metal-atom masses, therefore this peak can be straightforwardly attributed to the alkali-metal substrate stretching mode.

In contrast to the previous case, the reconstructed surface, Na/Cu(110) at 300 K, shows *two* energy-loss features, one again at 18 meV and another one at about 11.5 meV (see, for example, Fig. 1, curve *e*). The energy of the 18-meV peak, on the reconstructed as well as on the unreconstructed surfaces, does not show any Θ dependence.

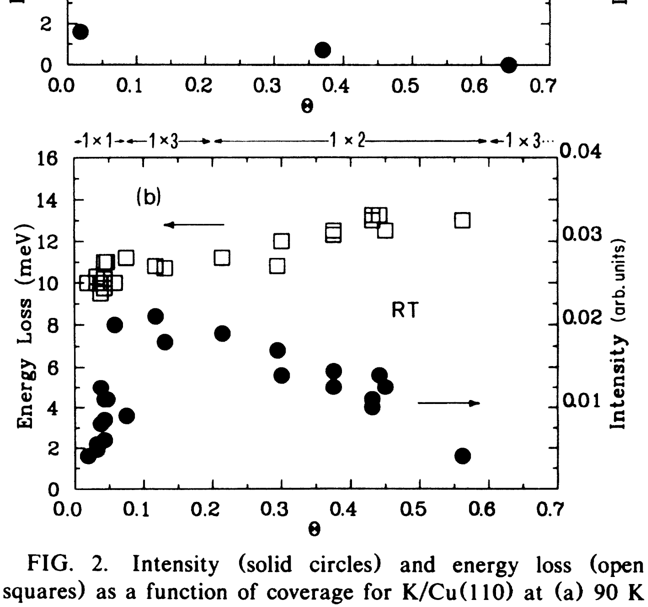

FIG. 2. Intensity (solid circles) and energy loss (open squares) as a function of coverage for K/Cu(110) at (a) 90 K and (b) RT.

The coverage dependences of the energy and relative intensity of the Na-induced peaks are not shown here because of the large uncertainty we have in the measure of the Na coverage. Within this uncertainty the intensity of the 18-meV peak follows the same behavior observed in the case of K. The 11.5-meV peak, characteristic of the reconstructed surface, is present at coverages lower than those at which the spots of the (1×3) and (1×2) reconstructions are observed in the LEED pattern.

The K HREELS spectra on reconstructed Cu(110) at 300 K seems to follow a different Θ dependence. At low coverages a strong broad peak appears at about 10 meV (see Fig. 1, curve *b*) and moves gradually, reaching approximately 13 meV at $\Theta \cong 0.4$ (Fig. 1, curve *c*). The energy and the intensity of this loss are plotted in Fig. 2(b) as a function of coverage Θ. In this figure we also indicate the surface reconstruction sequence we observed by LEED at RT, which is in good agreement with that reported by Fan and Ignatiev.[2] At RT the energy of the K-induced energy-loss feature stays constant (within 1 meV) when the first extra spots appear in the LEED pattern at $\Theta \cong 0.08$ and then shifts gradually towards higher values with increasing coverage. We also observed that when the sample is dosed to $\Theta = 0.15$ at 90 K and then heated to 300 K, the peak shifts from 14 to 11 meV and the substrate reconstructs. On cooling back, the vibrational frequency remains constant and reconstruction is preserved.

Both the K and Na data show that the reconstructed surfaces are characterized by an alkali-metal-induced peak which lies at an energy appreciably lower than that measured on the unreconstructed surfaces. This feature persists down to the lowest coverage we studied ($\Theta_K = 0.02$), pointing to local reconstruction even when no extra spots are observed in the LEED pattern (i.e., no long-range order). This finding is in agreement with the results of work-function studies of the Cs/Ag(110) system[5] and LEED studies of Cs and K on Cu(110).[2]

The vibrational spectra of the Na-covered surface at 300 K show two dipole-active modes. Both are present at all coverages, i.e., even when all the surface is completely reconstructed [$\Theta \geq 0.1$ (Refs. 4 and 8)]. This fact rules out the possibility that one of the two peaks is related to alkali-metal atoms in the troughs of reconstructed regions and the other one to Na atoms in unreconstructed parts of the surface. We attribute the higher-energy peak (18 meV) to the Na—Cu stretching mode because its frequency is the same as that of the peak observed on the unreconstructed surface. The low-energy peak, which is clearly associated with reconstruction (being absent at 90 K), can be attributed to a copper surface mode which becomes highly dipole active in the presence of the alkali-metal atoms. This substrate mode, which should appear at nearly the same energy on the K-covered surface, would also explain why the K-induced peak on the reconstructed surface shifts from 10 to 13 meV with increasing coverage. This shift is, in fact, in contrast with the absence of a coverage-dependence of the stretching mode of Na on reconstructed Cu(110), but it can be understood if one assumes that the K-induced structure results from the unresolved contributions of both the K—Cu stretching mode (at an energy close to that observed on the unreconstructed surface) and the Cu surface mode (at about 10 meV). The center of this peak would then shift in energy either because the relative intensities of the two components change or because the energy of the substrate mode changes with potassium coverage and/or the type of surface reconstruction. According to the first picture the Cu mode contribution would dominate at low coverages and would become much less important at high coverages. This is supported by the coverage dependence of the full width at half maximum of the K-induced loss: it first increases roughly linearly from 5 meV at very low coverages to 10 meV at $\Theta = 0.15$ and then again decreases to 5 meV. However this interpretation does not seem to be confirmed by preliminary data measured on the Na-covered surface which show that the ratio of the intensities of the two losses changes by no more than a factor of 2 as a function of coverage.

We are not able to discriminate between the two models because our data do not allow us to measure with sufficient precision the coverage dependence of the energies of the substrate mode on the Na/Cu(110) surface.

In order to be detected by HREELS in the specular geometry, this surface mode must be at the Γ point[9] if the surface is well ordered. In the case of a (1×3) and a (1×2) well-ordered reconstruction, this mode could derive from the S_3 surface mode of the unreconstructed surface in the ΓY [001] direction.[10] In fact, by folding the surface Brillouin zone, dipole-active modes at point Γ are obtained at about 11 meV for both reconstructions. The substrate motion associated to this mode[11] is sketched in Fig. 3. An alkali-metal atom placed in the trough position of the reconstructed surface should oscillate vertically in response to the Cu motion and produce a large oscillating dipole field. However, the 11.5-meV mode is detectable also when no long-range order in the [001] direction is present. In this case its energy is mainly determined by that of the singularity of the density of states of the S_3 mode [at about 12 meV on clean Cu(110)]. The large width of the 11.5 meV mode, also on (1×2) and (1×3) reconstructed surfaces, can be explained as an effect of one-dimensional disorder. Such a one-dimensional disorder in the direction perpendicular to the chain orientation (ΓY) has been found for the Au(110)-(1×2) reconstructed surface.[12]

The broad resonant mode at $\mathbf{k}=\mathbf{0}$, which falls at about 20 meV on clean Cu(110) (oscillation of the first layer with respect to the second layer[6]) is not observed in our spectra when the surface is dosed with K or Na, but very likely it is buried under the tail of the alkali-metal–stretching energy loss. This mode is not enhanced by the presence of the adsorbates possibly because it does not affect the dipole that builds up between the Cu surface and the alkali-metal overlayer.

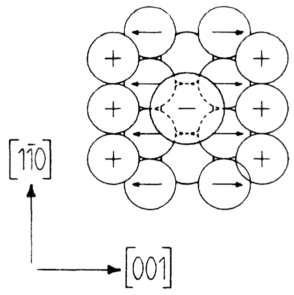

FIG. 3. Displacement associated with the phonon at 11.5 meV of the reconstructed surface. The alkali-metal atom (bigger circle) is pushed up and down by the motion of the Cu atoms.

As seen in Fig. 2, both on the reconstructed as well as on the unreconstructed surfaces, the energy-loss intensity increases linearly up to $\Theta \cong 0.1$ and then sharply decreases, showing that the dynamical dipole moment per adatom is constant in the low-coverage range, and then diminishes for $\Theta > 0.1$.[13] This coverage is close to that at which the static dipole moment per atom also begins to drop, as shown by work-function measurements.[14] The Θ dependence of the dynamical dipole moment (see Fig. 2), and the static dipole moment[14] point to a large charge redistribution for $\Theta \cong 0.1$ (i.e., $\frac{1}{6}$ of the saturation coverage) for potassium on both reconstructed and unreconstructed Cu(110). A sharp maximum of the loss intensity at $\frac{1}{6}$ of the saturated monolayer has also been observed for K on Cu(100) and Cu(111) and for Na on Cu(100).[7] The fact that we find the same coverage dependence of the loss intensity also for the reconstructed Cu(110) surface indicates that the charge redistribution is mainly determined by the lateral interaction of the adsorbates and that it is not substantially influenced by the reconstruction. Additional support for this conclusion comes from the study of the coverage dependence of the binding energy of the K $3p$ level measured by EELS.[15] Also in this case the data taken on the reconstructed and the unreconstructed surfaces are substantially similar, showing both a 0.4-eV decrease of the binding energy from lowest coverage up to $\Theta \cong 0.2$ and a constant value for higher coverages.

In conclusion, the vibrational spectra of K and Na on Cu(110) show that local surface reconstruction explains the appearance of a second energy loss at coverages as low as $\Theta \cong 0.02$. The new dipole-active mode derives from surface phonons dispersed along the ΓY direction of the Brillouin zone of the clean Cu surface. Moreover, the charge redistribution which takes place for $\Theta \cong 0.1$ does not depend on reconstruction but is solely due to lateral interaction between adsorbates.

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