

Unusual chemisorption behavior of Te on Cu {111} versus Cu {100}

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Surface extended x-ray absorption fine-structure measurements of Te chemisorbed on Cu {111} and Cu {100} surfaces show the adsorbate structures to be remarkably different. Unlike the overlayer occupation of Te in the highest-symmetry hollow sites found here for Cu {100}, the data for Cu {111} indicate *substitutional* displacement by Te of surface Cu atoms.

From the atomic adsorbate structures on low index metal surfaces studied thus far with low-energy-electron diffraction (LEED),¹ the general rule has emerged that adsorbates can be simply regarded as hard spheres occupying highest-symmetry metal hollow sites. The two known exceptions to this rule involve comparatively small, chemically reactive, low Z adsorbates, viz., Ti {0001}-(1 × 1)-N, where N resides between the first and second Ti layers,² and Ni {110}-(2 × 1)-O, where O occupies the short bridge site.³ In this work we report on surface extended x-ray absorption fine-structure (SEXAFS) measurements which also violate this picture but which involve a very different type of adatom, Te, chemisorbed on Cu {111}. Our results suggest that Te occupies a novel nearly substitutional site replacing Cu atoms *within* the surface layer. This chemisorption behavior is similar to that observed in the early stages of subsurface oxidation of W {110}, Ni {111}, Ni {100}, and Ni {110} surfaces⁴ but is unusually surprising for Te in view of its large relative size, its comparatively low chemical reactivity, and the occupation of conventional fourfold hollow sites determined here for Te on Cu {100}. Implications of our results in terms of bond lengths, bond order, and complementary measurements are discussed.

The SEXAFS experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) using equipment previously described.⁵ At base pressures of $\leq 1 \times 10^{-10}$ Torr, Te vapor was directionally deposited onto specular room-temperature surfaces previously cleaned and characterized by Auger and LEED spectroscopies. The sharp $p(2 \times 2)$ and $(2\sqrt{3} \times \sqrt{3})R30^\circ$ patterns for the Te-covered {100} and {111} surfaces remained unchanged after annealing at $\sim 350^\circ\text{C}$ for ~ 5 min. Coverages were consistent with $\Theta = \frac{1}{4}$ and $\frac{1}{3}$ monolayers, respectively, determined by Auger spectra from these and previous I overlayer systems.⁵ SEXAFS measurements from the Te L_{III} edge were taken in the total yield mode as a function of angle θ , measured between the synchrotron polarization \vec{e} and the surface normal. For Te/Cu {111} the measurements were reproduced

using a different {111} crystal and Te Auger electron detection.^{5(a)}

In Fig. 1 we compare identically analyzed data from the {100} and {111} Te-covered surfaces. Details of the analysis procedures have been reported elsewhere.^{5,6} The upper panel shows the background-subtracted raw data⁷ taken at $\theta = 90^\circ$ and the lower panel shows the back-transformed filtered data of the first nearest-neighbor (NN) contribution to the total SEXAFS spectrum.^{5,6} Also in the lower panel are shown the filtered back-transformed data at $\theta = 40^\circ$, 20° for the {100}, {111} systems. The polarization dependences of the SEXAFS amplitudes in these systems are *opposite* to one another, giving direct evi-

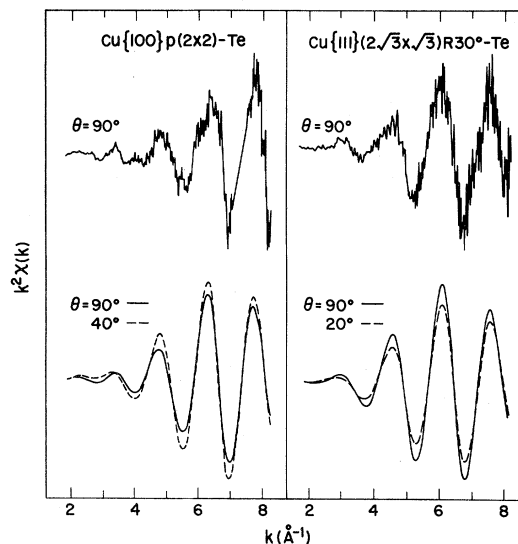


FIG. 1. Upper: Background-subtracted raw SEXAFS data multiplied by k^2 . Lower: Polarization-dependent filtered data of first nearest neighbors. Filtered data were obtained using window functions spanning 1.2–3.4 Å around the dominant Te-Cu peak in the Fourier transformed data (not shown). The intensity scales (arbitrary) are different for the raw and filtered data and for the {111} and {100} surfaces; see Table I for normalized values.

TABLE I. Calculated vs experimental N_S values for Te/Cu{100} and Te/Cu{111}.

	θ	Atop	Bridge	Hollow	Subst.	Expt. ^a
Cu {100}:	40°	1.2	2.3	4.3	3.6	3.9 ± 0.7
	90°	0.7	1.6	3.7	4.5	3.2 ± 0.6
	40°/90°	1.7	1.4	1.2	0.8	1.2 ± 0.1
Cu {111}	20°	1.5	2.7	3.8	4.9	5.4 ± 1.0
	90°	0.7	1.6	2.5	6.6	7.0 ± 1.3
	20°/90°	2.1	1.7	1.5	0.7	0.8 ± 0.1

^a See text with reference to error bars.

dence that the Te–Cu bonds are oriented very differently with respect to the surface. We now quantify this result.

The first NN bond lengths in the surface systems, R_1 , are determined using the phase shift of the model compound Cu_2Te and the assigned Te–Cu distance of 2.667 Å.⁸ Allowing ± 0.04 Å uncertainty in the actual Te–Cu distance in this compound,⁹ we obtain $R_1 = 2.62 \pm 0.04$ Å for Te–Cu {100} and 2.69 ± 0.04 Å for Te–Cu {111}. For both systems the individual measurements taken at two different θ values agreed with each (i.e., independent of model compound) to better than ± 0.005 Å.

The effective surface atom coordination numbers N_S for different θ values are determined⁹ with respect to $N = 4$ in Cu_2Te and are compared in Table I with the calculated absolute amplitudes (in terms of N_S) assuming Te occupation in the highest-symmetry sites of Cu {100} and Cu {111} according to¹⁰

$$N_S \approx \frac{3}{2} \sum_i (1.4/3 + 0.6|\bar{\epsilon} \cdot \bar{r}_i|^2)$$

The results for Cu {100} show that only the fourfold hollow site is consistent with our measurements, in agreement with an earlier LEED study.¹¹ Confirmation of this is provided by comparing the experimental and calculated relative amplitudes (i.e., the ratios), which avoids the uncertainties in absolute amplitudes introduced by reference to the model compound^{5(b)} (this explains the smaller quoted errors). We see that Te adsorption on Cu {100} is well described in terms identical to that for I (Ref. 5) and for other chalcogens on this and similar {100} surfaces.^{1,3,11}

The amplitude data of Te on Cu {111} at $\theta = 90^\circ$ is greater than that at $\theta = 20^\circ$, necessarily implying that the Te–Cu{111} bond is oriented predominantly within the surface plane. The unreconstructed closepacked {111} surface cannot accommodate this condition without atomic rearrangement, and the simplest one appears to be substitutional displacement of $\frac{1}{3}$ monolayer surface Cu atoms by Te.¹² The resulting over-

layer structure is shown in Fig. 2 along with the structure determined here for Cu {100}- $p(2 \times 2)$ -Te. Comparison of both the absolute and relative calculated amplitudes of our suggested model with the corresponding experimental values (see Table I) shows the agreement to be very good. Note that our short-range structural model does not attempt to account for the observed $(2\sqrt{3} \times \sqrt{3})R30^\circ$ pattern, but instead predicts a simple $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern. The doubled unit cell size could be explained either by nearly substitutional Te dimerization, surface or subsurface buckling, previously displaced Cu adatom decoration, or a combination of these factors. Our present data cannot distinguish between these possibilities. Despite the lack of a complete picture for describing the long-range properties of Cu {111}- $(2\sqrt{3} \times \sqrt{3})R30^\circ$ -Te, however, the extremely isotropic first NN bond length and the very good absolute and relative agreement seen in Table I both support the essential validity of the short-range features of our proposed model.

A strength and weakness of the SEXAFS technique is its ability to determine only short-range structural

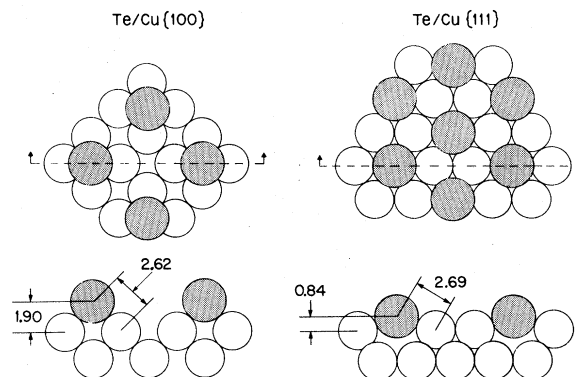


FIG. 2. Top and side views of overlayer structures for Te (shaded) on Cu {100} and Cu {111} surfaces.

information. Second and higher NN bond lengths up to $\sim 5 \text{ \AA}$ have been easily observed in bulk⁶ and surface¹³⁻¹⁵ EXAFS measurements in which the number of scattering atoms, their vibrational properties, their backscattering probabilities, and the statistical quality of the data were all favorable. Despite the comparable statistical quality of the present data to these other SEXAFS studies,¹³⁻¹⁵ reliable second or third NN substrate bond lengths were nevertheless not observed, a situation similar to that found for I on Ag{111}, Cu{111}, and Cu{100}.⁵ From comparison with SEXAFS data from Ni{100}-c(2 × 2)-S (Ref. 13) and Cu{100}-c(2 × 2)-Cl (Ref. 14), we attribute this result to vibrational damping between the substrate and higher Z (more weakly bound) Te and I adsorbates. This unavoidable short-range limitation¹⁶ implies that additional measurements of Cu{111}-(2√3 × √3)R 30°-Te using techniques more sensitive to long-range properties, e.g., LEED, surface x-ray scattering, or high-energy ion backscattering with blocking, would provide important complementary information on this interesting overlayer structure.

Based on a small sampling of LEED and SEXAFS data, a previous study suggested^{5(b)} that halogen-metal surface bond lengths may be generally longer than those in the stable bulk analogs whereas chalcogen-metal surface bond lengths may be generally shorter. Our new SEXAFS results for Cu{100}-p(2 × 2)-Te, along with those for Ni{100}-c(2 × 2)-S (Ref. 13) and Cu{100}-c(2 × 2)-Cl,¹⁴ are consistent with these conclusions. This remains so despite the fact that the new SEXAFS bond lengths are larger relative to the earlier LEED results, viz., $2.62 \pm 0.04 \text{ \AA}$ vs $2.48 \pm 0.10 \text{ \AA}$ (Ref. 11) for Te-

Cu{100} and $2.23 \pm 0.02 \text{ \AA}$ (Ref. 13) vs $2.19 \pm 0.06 \text{ \AA}$ (Ref. 17) for S-Ni{100}. Because this surface versus bulk bond length trend only considers surface data in which the conventional highest-symmetry metal hollow sites are occupied, it is not surprising that R_1 in the Cu{111}-(2√3 × √3)R 30°-Te structure does not obey this trend. It has also been pointed out^{5(b)} that, in general, $X-M\{111\}$ bond lengths are shorter than those of $X-M\{100\}$ assuming conventional site occupation. Following Madhukar,¹⁸ this is due to the increased bond order in the threefold versus fourfold coordinated systems. Within this framework of correlating bond length (strength) with bond order, the atypically longer Te-Cu{111} bond length relative to Te-Cu{100} provides additional support for the increased sixfold versus fourfold coordination proposed in our model of Cu{111}-(2√3 × √3)R 30°-Te.

In summary, we have found very different chemisorption behavior for submonolayer coverages of Te on Cu{111} vs Cu{100} surfaces. An unusual overlayer structure is proposed for Te on Cu{111} which differs from all previously reported adsorbate-metal structures involving medium- or high-Z adatoms. Additional measurements using complementary techniques are required to characterize its long-range properties and to understand the driving force(s) responsible for its occurrence.

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