Are Surface-Atom Vibrational Amplitudes along the Normal Always Larger than in the Plane?

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Temperature- and polarization-dependent surface extended x-ray absorption fine-structure measurements from higher-neighbor shells are used to study the anisotropy of surface vibrational amplitudes. In Cu(100)$c(2\times2)$-Cl, mean square displacements of both Cl and surface Cu atoms are found to be approximately twice as large within the surface as along the normal. This anisotropy is opposite to that reported in recent experimental and theoretical studies of other systems.

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Several studies have recently addressed the existence of anisotropic vibrational amplitudes of surface atoms. This general problem of surface dynamics reflects the shape of the surface potential and is directly related to diffusion, desorption, surface reactions, and epitaxial growth.[1] Theoretical calculations[2] of H on Ru(0001) and Pt(111) showed that, contrary to previous vibrational-mode assignments, the smoothing of electronic charge at a metal surface enhances the H in-plane motion relative to its perpendicular motion. This picture for H atoms, however, is opposite to the conventional view usually held for clean metals that perpendicular surface-atom vibrational amplitudes should be larger because of the increased degrees of freedom at the surface. Indeed, recent ion-scattering[3] and theoretical[4,5] studies of not only clean metals, but surface extended x-ray absorption fine structure (SEXAFS)[5,6] results from adsorbate-covered surfaces as well, all concur with the conventional view.

In this Letter we report on temperature- and polarization-dependent SEXAFS measurements from the Cu(100)$c(2\times2)$-Cl surface. Our data show that the relative surface-atom motions within the plane are almost twice as large as those along the normal. We propose that the transfer of charge between the adatom and substrate is primarily responsible for the reversed vibrational anisotropy of clean versus adsorbate-covered surface atoms. The sharp contrast of our results with the conclusions reached in previous SEXAFS work,[5,6] using first-neighbor shells, are explained in terms of correlated motions. The general procedures described here for determining anisotropic surface-vibrational amplitudes involve reliable measurements of higher-neighbor shells. With such SEXAFS data, correlation effects are minimized, making it straightforward to extract otherwise difficult but important information related to the nature of the surface potential.

At temperature T, the SEXAFS $\chi_i(k)$ from a K or L_1 edge of an absorbing atom surrounded by N_i neighbors at a distance r_i is given by[7]

$$\chi_i(k,\theta,T) = -\sum_j^{N_i} 3\,|\epsilon_\theta\cdot\mathbf{r}_{0ij}|^2 f_i(\pi,k)(kr_i^2)^{-1} e^{-2r_i/\lambda_i(k)} \sin[2kr_i+\phi_i(k)]\, e^{-2k^2\sigma_i^2(T)}, \tag{1}$$

where ϵ_θ is the x-ray polarization at angle θ relative to the surface normal, $\mathbf{r}_{0ij}$ is the unit vector connecting the jth neighbor in the ith shell to the central absorbing atom at equilibrium position $\mathbf{r}_0$, $f_i(\pi,k)$ is the backscattering amplitude, $\lambda_i(k)$ is the electron mean free path, and $\phi_i(k)$ is the total phase shift. The last term is the SEXAFS Debye-Waller factor (DWF) for harmonic oscillators, with $\sigma_i^2(T)$ being the mean square *relative* displacement along $\mathbf{r}_{0ij}$. This quantity is related to the individual mean square displacements $\langle u_i^2(T)\rangle$ and $\langle u_0^2(T)\rangle$ measured by x-ray diffraction via[8]

$$\sigma_i^2(T) = \langle u_0^2(T)\rangle + \langle u_i^2(T)\rangle - 2\langle u_0(T)u_i(T)\rangle, \tag{2}$$

where $\mathbf{r}_{ij} = \mathbf{r}_0 + \mathbf{u}_{ij} - \mathbf{u}_0$, $u_0 = \mathbf{u}_0\cdot\mathbf{r}_{0ij}$, and $u_i = \mathbf{u}_i\cdot\mathbf{r}_{0ij}$. The correlated motion between the absorbing atom and the atoms in the ith shell, expressed by the third term, is obviously important for first neighbors ($i=1$) because of their direct bonding, while it is much less important for neighbors at larger distances.

It follows from Eq. (2) that the anisotropic displacement of surface atoms can be best determined with SEXAFS by comparison of the DWF from two different shells whose distances are nearly parallel and perpendicular to the surface. Such a comparison is meaningful, however, only if the backscattering atoms are identical and they are not directly bonded to the absorbing atom. In this way artifactual effects due to differences in mass and correlated motion are minimized. These considerations governed the analysis of the system studied here.

The Cu(100)$c(2\times2)$-Cl surface was prepared on a stress-free electropolished Cu(100) crystal by procedures described previously.[9] Cl K-edge SEXAFS data were measured at the Stanford Synchrotron Radiation Laboratory by monitoring of the Cl $K\alpha$ fluorescence yield.[10] SEXAFS amplitudes from in-plane and out-of-plane coordination shells were emphasized by orientation of the sample relative to the x-ray polarization. Reproduci-

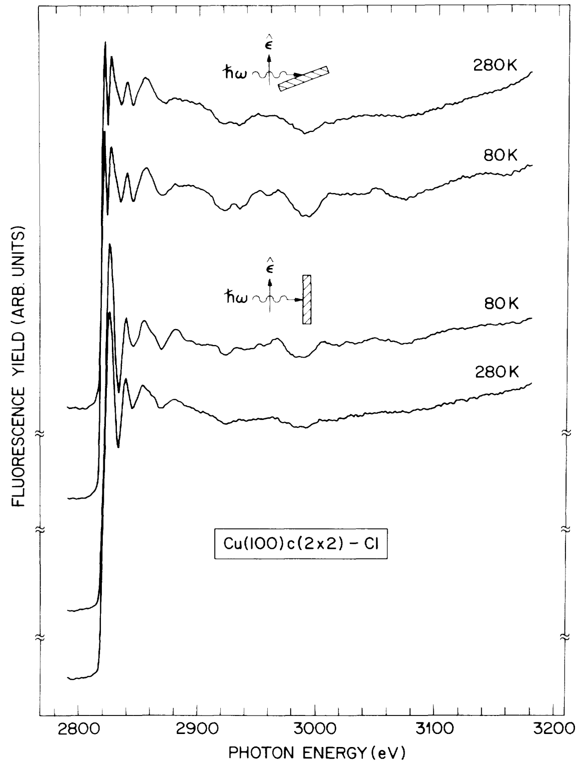

FIG. 1. Raw Cl K-edge absorption data from 0.5 monolayer of Cl on Cu(100) taken at 80 and 280 K, with the electric field ϵ_θ parallel ($\theta=90°$) and nearly normal ($\theta=20°$) to the surface.

bility of all measurements was checked by our performing them twice on independently prepared surfaces.

Figure 1 shows the raw K-edge data taken with ϵ_θ parallel ($\theta=90°$) and nearly perpendicular ($\theta=20°$) to the surface at temperatures 80 and 280 K. The strong dependence of the SEXAFS signal on polarization and temperature is evident. The Fourier transforms of the background-subtracted $k\chi(k)$ data at 80 K are shown in Fig. 2. Peak assignments are given in the caption. In addition to confirming the fourfold hollow chemisorption geometry for Cl[9,11] (see inset in Fig. 2), the higher-quality data here also allow for the reliable determination of r_2 and r_3.[12] The results are summarized in Table I. While r_3 gives the Cl-Cl distance in excellent agreement with the Cu lattice parameter ($a_0=3.615$ Å), r_2 is 0.09 ± 0.02 Å larger than the value expected from r_1 and the ⟨100⟩ interlayer spacing. This is a straightforward and very accurate measurement of the Cl-induced expansion, $(5\pm1)\%$, between the first and second Cu(100) planes. The implied weakening of the corresponding interlayer Cu bonds will be used below in our discussion of the observed anisotropic surface-atom displacements.

The procedure used to evaluate the relative displacements of different Cl-Cu shells relies on the temperature dependence of the DWF in $\chi_i(k,\theta,T)$. From Eq. (1), the logarithmic ratio of SEXAFS measurements for the ith shell taken at temperatures T_1 and T_2 is[13-15]

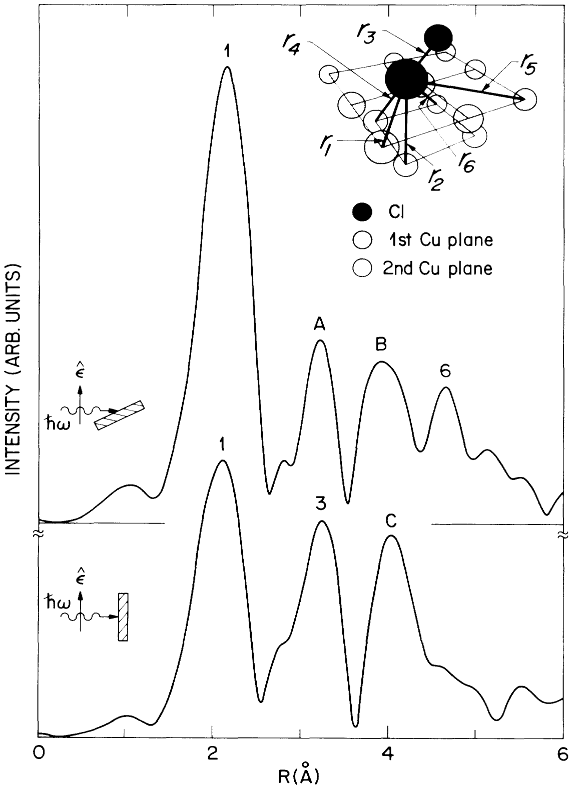

FIG. 2. Fourier transforms of 80-K data shown in Fig. 1. The SEXAFS χ_i from the first six coordination shells at distances r_i around the absorbing Cl atom (see inset) constitute the labeled peaks as follows: 1, χ_1; A, $0.88\chi_2+0.12\chi_3$; 3, χ_3; B, $0.64\chi_4+0.36\chi_5$; C, $0.83\chi_5+0.17\chi_4$; 6, χ_6.

$$\ln\left[\frac{\chi_i(k,\theta,T_1)}{\chi_i(k,\theta,T_2)}\right]=2k^2[\sigma_i^2(T_2)-\sigma_i^2(T_1)]$$
$$=2k^2\Delta\sigma_i^2. \qquad (3)$$

$\Delta\sigma_i^2$ is a measure of the change in thermally excited

TABLE I. Summary of SEXAFS r_i's and $\Delta\sigma_i^2$'s.

i	N_i	r_i(expt) (Å)	r_i(calc)[a] (Å)	$\Delta\sigma_i^2$ (10^{-3} Å^2)
1	4	$2.37\pm0.01_5$	⋯	5.5 ± 0.5
2	1	3.43 ± 0.02	⋯	6.5 ± 1
3	4	$3.62\pm0.01_5$	3.62	10 ± 2
4	4	4.25 ± 0.03	4.28	9 ± 2
5	8	4.31 ± 0.02	4.32	12.5 ± 1
6	4	5.05[b]	4.98	⋯

[a] Calculated with r_1(expt), r_2(expt), and a_0(Cu).

[b] Multiple scattering from first-neighbor Cu atoms affects this value, evident in the anomalously large E_0 shift from the CuCl model compound.

motions between the absorbing and ith-shell scattering atoms. Provided correlated motions are negligible, comparison between $\Delta\sigma_i^2$ and $\Delta\sigma_l^2$ gives direct information about the relative displacement of atoms in the ith and lth shells. This comparison is meaningful because possible differences in $\lambda(k)$, static disorder, or other spurious effects between the different shells are automatically canceled.

We have applied Eq. (3) to the SEXAFS $\chi_i(k,\theta,T)$ for the individual shells $i=1$–5 at 80 and 280 K. The shells at distances r_2, r_4, and r_5 were isolated by use of appropriately weighted linear combinations of data taken at different polarizations. We first consider $\chi_2(k,\theta,T)$ and $\chi_5(k,\theta,T)$, which are comprised of Cu atoms not bonded to Cl, lying along directions perpendicular and nearly parallel to the surface, respectively. Results for these shells are shown in Fig. 3. The linearity of the plots confirms the validity of Eq. (3) and allows for the determination of $\Delta\sigma_2^2=(6.5\pm1)\times10^{-3}$ Å^2 and $\Delta\sigma_5^2=(12.5\pm1)\times10^{-3}$ Å^2. The quoted uncertainties include the reproducibility of our SEXAFS measurements from different samples (precision) and the systematic errors associated with our analysis methods (accuracy). The clear difference between $\Delta\sigma_2^2$ and $\Delta\sigma_5^2$ reveals the presence of a strong anisotropy in the surface-atom motions. The relative displacements nearly along the surface are almost *twice* as large as those along the normal.

The values of $\Delta\sigma_5^2$ and $\Delta\sigma_2^2$ compare the nearly parallel Cl–surface-Cu relative displacements to the perpendicular Cl–second-layer Cu relative displacements, and so must contain differences between the individual surface-Cu and second-layer–Cu motions. Therefore, it could be argued that the perpendicular Cl–surface-Cu relative displacements, which cannot be directly probed in our measurements, still have the largest amplitude. Below we show that our determined values of $\Delta\sigma_i^2$ for $i=1$, 3, and 4 (see Table I) lead to two conclusions which, combined, rule out this possibility.

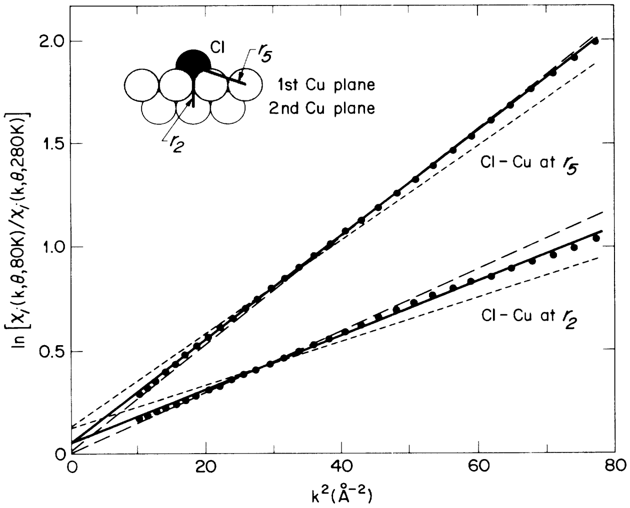

FIG. 3. Results of Eq. (3) for Cl SEXAFS χ_2 and χ_5 from Cu shells at r_2 and r_5 (see inset) with $T_1=80$ K and $T_2=280$ K. The slopes $2\Delta\sigma_2^2$ and $2\Delta\sigma_5^2$ of the linear least-squares fits (solid lines) to the data (dotted lines) determine the values given in Table I. These fits are applied to data analyzed with window-filter widths of 1.2 Å. The long- and short-dashed lines show correlated changes in fitting of the data obtained with window widths of 1.4 and 1.0 Å, respectively. Such procedures exemplify systematic errors which are incorporated in the uncertainties quoted for $\Delta\sigma_i^2$.

(1) The correlation term $2\Delta\langle u_0u_1\rangle$ is large: The perpendicular Cl–surface-Cu relative displacements contained in $\Delta\sigma_1^2$ are unfortunately obscured by the presence of correlated motion. It is possible to estimate the magnitude of the first-neighbor correlation term by projecting the uncorrelated relative displacements of the fifth-shell atoms lying along $\mathbf{r}_{05}$ onto $\mathbf{r}_{01}$ (which are at angles 69.2° and 49.7° to the normal, respectively). The result,

$$\delta=\Delta\sigma_5^2\cos^2(69.2°-49.7°)=(11.4\pm1)\times10^{-3}\ \text{Å}^2,$$

provides a minimum value of $\Delta\langle u_0^2\rangle+\Delta\langle u_1^2\rangle$ because the contribution from motions perpendicular to $\mathbf{r}_{05}$ have been ignored. The difference $\delta-\Delta\sigma_1^2=(5.9\pm1.5)\times10^{-3}$ Å^2 is therefore a lower limit for the correlation term $2\Delta\langle u_0u_1\rangle$. This value is nevertheless large, being greater than the corresponding value in bulk Cu,[14] 3.6×10^{-3} Å^2. The strong Cl-Cu correlated motion, coupled with the Cu(100) interlayer expansion, is consistent with a picture of strong Cl-Cu bonding arising from donation of surface-Cu charge to Cl.

(2) $\Delta\langle u_{\rm Cl}^2\rangle_\parallel$ is larger than $\Delta\langle u_{\rm Cl}^2\rangle_\perp$: $\Delta\sigma_4^2$, which describes relative Cl–second-layer Cu relative displacements at angles 36.9° to the normal, is larger than $\Delta\sigma_2^2$. Assuming that second-layer Cu mean square displacements in Cu(100) are isotropic, this result implies that Cl displacements in the plane are larger than those along the normal because contributions of parallel displacements are contained in $\Delta\sigma_4^2$, but not in $\Delta\sigma_2^2$. Alternatively, using $\Delta\sigma_2^2$ and assuming that second-layer Cu perpendicular mean square displacements are similar to those of bulk Cu,[14] $(4.2\pm0.5)\times10^{-3}$ Å^2, we estimate

$$\begin{aligned}\Delta\langle u_{\rm Cl}^2\rangle_\perp&=(6.5-4.2)\times10^{-5}\ \text{Å}^2\\&=(2.3\pm1.5)\times10^{-3}\ \text{Å}^2.\end{aligned}$$

This value is indeed smaller by a factor of 2 than $\Delta\langle u_{\rm Cl}^2\rangle_\parallel=(5\pm1)\times10^{-3}$ Å^2 determined from $\Delta\sigma_3^2$.[16]

The above results, showing strong correlated motion between Cl and first-neighbor Cu atoms and anisotropic mean square displacements for Cl analogous to the anisotropy revealed by $\Delta\sigma_2^2$ and $\Delta\sigma_5^2$, collectively suggest that the surface Cu atoms must follow the anisotropic motion of the surface Cl atoms. This, in turn, indicates that the surface Cu atoms have vibrational amplitudes along the surface that are larger than those along the normal. We propose that the origin of the anisotropy between normal and parallel mean square displacements for both Cl and Cu surface atoms is connected with the transfer of charge from surface Cu to chemisorbed Cl. Such charge transfer is expected to induce a stiffening of the effective perpendicular Cl-Cu force constant, as reported for H on Ru(0001) and Pt(111),[2] a softening of the in-plane surface vibrational modes due to weakening of the Cu-Cu surface bonds, as in a recent study of O on Pt(111),[17] and an interlayer Cu(100) expansion, in agreement with our observation.

The trend of surface vibrational amplitudes found here is opposite to that reported in a previous SEXAFS study of Co on Cu(111).[5] The disagreement is traceable to differences in bonding and in correlated motion between in-plane Co-Co first neighbors and out-of-plane Co-Cu first neighbors.[18] The softer Co-Cu bond and the static disorder associated with the incommensurate Co monolayer[19] both account for $\Delta\sigma^2_{\text{Co-Cu}} > \Delta\sigma^2_{\text{Co-Co}}$. The importance of correlated motion was appreciated in the study of O on Cu(110).[6] There, differences in DWF's between the three observed O-Cu shells obtained at the same temperature were obscured by such correlations and could not provide definitive evidence for anisotropic surface displacements. Finally, the strong anisotropy reported on clean W(110),[3] with mean square displacements along the normal being larger than in the plane, is decidedly different from our results. Interlayer expansion due to charge transfer, present in the Cl/Cu(100) system but absent in W(110),[3] undoubtedly plays a role in the different surface-vibrational motions. Moreover, the different relative number of in-plane versus out-of-plane metal bonds for the two surfaces must also be considered. A substantive understanding of these two effects, however, must clearly await additional theoretical and experimental studies as a function of temperature, substrate, adsorbate, and coordination geometry.

In conclusion, we report SEXAFS measurements from Cu(100)$c(2\times2)$-Cl which reveal anisotropic displacements of both Cl and Cu surface atoms. Their vibrational amplitudes are about 2 times larger in the surface than along the normal. The presence of very large correlated motion between Cl and directly bonded Cu atoms was also demonstrated. A general procedure involving temperature- and polarization-dependent SEXAFS measurements of higher shells was outlined for evaluating the anisotropy of surface vibrational motion. The results found here for Cl on Cu(100) are opposite to those reported for several other systems and demonstrate the need for testing our proposed charge-transfer model with further systematic study.

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