Experimental and Theoretical Evidence for a Strong Anisotropy of the Surface Debye-Waller Factor as Determined for a Monolayer of Cobalt on Copper (111) by Surface Extended X-Ray-Absorption Fine Structure

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We present here the first determination of the anisotropy of the surface Debye-Waller factor involved in a surface extended x-ray-absorption fine-structure (SEXAFS) experiment. It is deduced by use of relative temperature-dependent amplitude functions for two different polarizations. The mean square relative displacements of atoms are calculated with an elaborate lattice-dynamical model, treated by a continued-fraction technique. The results are in good agreement which shows the ability of SEXAFS as a valuable tool for the study of surface vibrations.

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In the harmonic approximation, the Debye-Waller factor which governs the temperature dependence of the damping of oscillations in surface extended x-ray-absorption fine structure (SEXAFS) is given by $\exp(-2k^2\sigma_j^2)$, where k is the photoelectron wave number and σ_j^2 the mean square relative displacement (MSRD) between the central atom (labeled 0) and its neighbor j: $\sigma_j^2 = \langle[(\mathbf{u}_0-\mathbf{u}_j)\cdot\mathbf{r}_{0j}]^2\rangle$, where $\mathbf{r}_{0j}$ is the bonding direction and $\mathbf{u}_0$ ($\mathbf{u}_j$) the displacement of atom 0 (j).[1,2] This factor has been studied for bulk metal both experimentally[1,3] and theoretically.[2,4] This Letter reports the first observations and calculations of the anisotropy of the MSRD at the surface in the case of a monolayer of cobalt on the (111) face of copper. Actually, even though this effect is already present for clean surfaces,[5] the presence of an adsorbed monolayer is required for the SEXAFS probe.[6]

The SEXAFS experiments were performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) on the DCI storage ring at Orsay with a Si(311) double-crystal monochromator. Measurements were made at a base pressure of 2×10^{-10} mbar. The copper (111) surface was cleaned by repeated cycles of argon-ion bombardment and annealing at 800 K; then cobalt was deposited at 300 K. The quality of the surface was monitored before and after the evaporation by LEED and Auger spectroscopy. It has been shown previously[7] that cobalt grows layer by layer under these conditions. Using Auger calibration, we estimate the coverage to be 1 ± 0.2 monolayer. The (1×1) LEED pattern of the clean surface of copper is conserved when the cobalt is adsorbed. In a previous part of this SEXAFS investigation,[8] from the polarization dependence, we have confirmed the two-dimensional character of this (1×1) Co/Cu(111) monolayer system and determined the surface bulk Co—Cu bond length as 2.47 ± 0.03 Å and the surface plane Co-Co distance as 2.51 ± 0.03 Å. Higher-coordination shell distances fit with expected fcc lattice positions.

The variations of the x-ray absorption coefficient of the sample were measured above the K edge of cobalt in the total-electron-yield mode. Experimental spectra at both 77 and 300 K are shown in Fig. 1(a) and relevant steps of the EXAFS analysis are displayed in Figs. 1(b)–1(d). The influence of the temperature on the damping of oscillations is clearly put forward by the decrease of their amplitude for large values of k.

The aim of the experiment was to compare the MSRD of the surface atoms in directions parallel and perpendicular to the surface. The highly anisotropic environment of surface atoms, which have lost half of the bonds perpendicular to the surface, heavily influences the vibrational modes and one expects vibrations perpendicular to the surface to have a larger amplitude than the parallel ones. We will show that SEXAFS with polarized light gives clear information on both MSRD.

The expression of the EXAFS modulations $\chi(k)$ for an atom in a discrete lattice with a Gaussian pair distribution function is proportional to

$$\sum_j \frac{3\cos^2(\theta_j)}{\bar{R}_j^2} e^{-2k^2\sigma_j^2} e^{-2\bar{R}_j/L} \times \sin[2k\bar{R}_j+\alpha(k)], \quad (1)$$

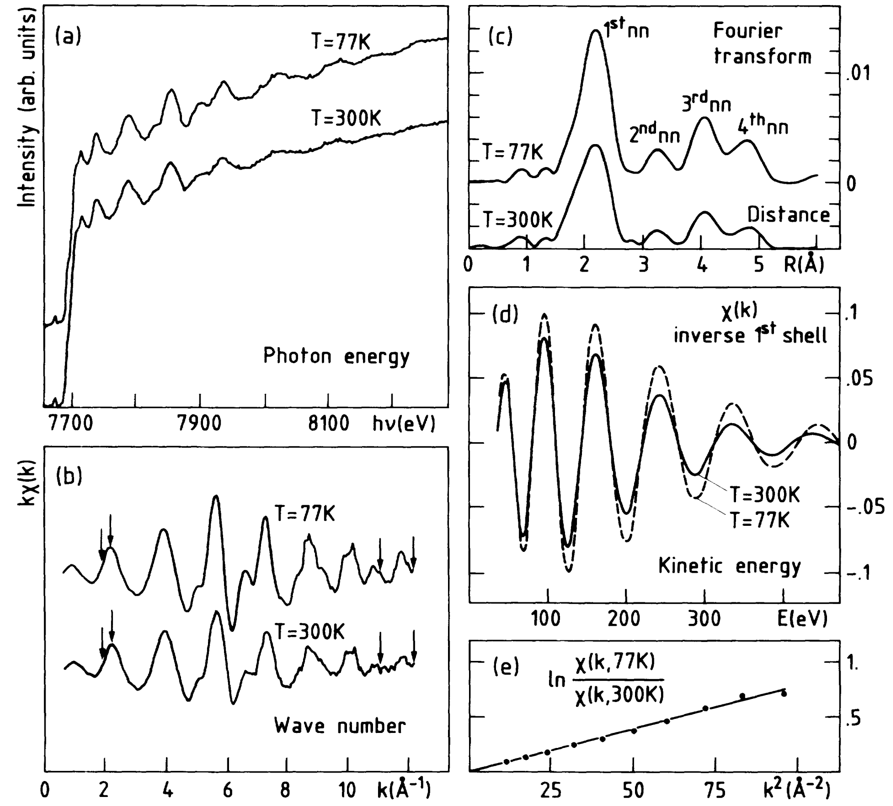

FIG. 1. (a) Experimental absorption spectra of a monolayer of Co on Cu (111) at the K edge of cobalt at both 77 and 300 K. The polarization of the light is parallel to the surface. (b) EXAFS modulations $[k\chi(k)]$ normalized to the height of the edge jump. The arrows indicate the limits of the cosine window used for the Fourier transform. (c) Fourier transforms of the spectra: The peaks corresponding to the first-, second-, third-, and fourth-nearest neighbors (nn) clearly appear. (d) Inverse Fourier transform of the first-neighbor peak. (e) Logarithm of the ratio of the amplitudes at 77 and 300 K as a function of k^2 for the first shell of neighbors. Points are the experimental data and the continuous line is the linear regression corresponding to these data.

where $\bar{R}_j$ is the mean distance between the central atom and the jth neighbor, σ_j^2 the corresponding MSRD, θ_j the angle between the jth bond and the polarization vector, $\alpha(k)$ the total phase shift, and L the electron mean free path. It is customary to use this formula in the interpretation of EXAFS spectra to determine the temperature dependence of the Debye-Waller factor in the case of isotropic systems.[1] Nevertheless, many systems with a small degree of disorder can be described with such a formula.[9] For disordered systems, it is necessary to take into account the high degree of anisotropy of the pair distribution function to obtain correct values of distances and coordination numbers as shown, for example, on Zn[2,9] (structural anisotropy), on Pt and Ir[10] (thermal disorder), and on the Ni (100) face.[11]

In the case of (1×1) Co/Cu(111), the ratio between the signal due to the adsorbate-adsorbate distance and the adsorbate-substrate distance is 9/1.5 when the polarization of the light is parallel to the surface and about $\frac{1}{9}$ when it is at 75° from the surface[8]: We thus separate the two different contributions. Therefore, despite the system anisotropy, it is justified to use formula (1) for each polarization. Moreover, since we are working at relatively low temperatures (77–300 K), we can assume only small deviations from the Gaussian distribution. This is justified by the fact that we observe no modification in the frequency of the EXAFS oscillations between 77 and 300 K [Fig. 1(d)]. Thus, we determine the variation of σ_j^2 between two temperatures by the ratio method (another kind of ratio method has already been used in SEXAFS[12]). For each polarization

$$\ln\left[\frac{\chi(k,\ T=77\ \mathrm{K})}{\chi(k,\ T=300\ \mathrm{K})}\right] = 2k^2[\sigma_j^2(T=300\ \mathrm{K}) - \sigma_j^2(T=77\ \mathrm{K})], \quad (2)$$

since all the other factors in Eq. (1) are strictly identical at 77 and 300 K. The power of this method is due to the simplicity of formula (2). We do not need any backscattering amplitudes and phase shifts determined from a model compound. Furthermore, the possible presence of some static disorder at the surface could damp the EXAFS oscillations and lead to a wrong determination of the Debye-Waller factor. This empirical procedure eliminates this effect since the static disorder is maintained when the sample is cooled.

In Fig. 1(e) we have represented $\ln[\chi(T=77\text{ K})/\chi(T=300\text{ K})]$ as a function of k^2. The linearity is well confirmed in the range 10–100 Å^{-2} of k^2 and justifies the use of formula (1). The slope of the line gives the variation of the MSRD parallel to the surface ($\Delta\sigma_{\parallel}^2$) between 77 and 300 K. Table I summarizes the results obtained in directions parallel and perpendicular to the surface ($\Delta\sigma_{\parallel}^2$ and $\Delta\sigma_{\perp}^2$) and these can be compared to those obtained for bulk cobalt and copper ($\Delta\sigma_{\text{Co}}^2$ and $\Delta\sigma_{\text{Cu}}^2$) under the same experimental conditions. Note that the bulk values of $\Delta\sigma_2$ are in good agreement with previous ones measured in transmission EXAFS.[13] As expected, there appears a significant anisotropy in the Debye-Waller factors: The MSRD of the surface cobalt atoms parallel to the surface is close to the bulk cobalt one while the MSRD normal to the surface is significantly larger ($\Delta\sigma_{\perp}^2/\Delta\sigma_{\parallel}^2 \sim 1.25$).

The present data give in a theory-independent fashion the temperature-dependent variations of the amplitudes of the dynamical relative displacements, both parallel and perpendicular to the surface, around the atomic positions of the unreconstructed (1×1) Co/Cu (111) surface. These results are complementary to those obtained by high-resolution electron-energy-loss spectroscopy which determines the surface phonon dispersion curves. The best related results can be found in the evaluation from LEED of mean square displacements of surface atoms larger than the bulk ones.[14] Note that this diffraction technique allows an estimation of absolute mean square displacements $\langle u^2\rangle$, and so the anisotropy ratios $\langle u_{\perp}^2\rangle/\langle u_{\parallel}^2\rangle$ of LEED and $\sigma_{\perp}^2/\sigma_{\parallel}^2$ of SEXAFS cannot be simply related: Beni and Platzman[2] have shown that the displacement correlation function which must be considered in EXAFS is of the same order of magnitude as the mean square displacement of atoms.

We have tested the generality of the above results by performing a calculation in the harmonic approximation, using a rotationally invariant lattice-dynamical model involving central forces between first- and second-nearest neighbors and angle-bending interactions between triplets of first neighbors.[15] The force constants are determined from experimental[16] elastic constants. In view of the small differences of Co and Cu lattice parameters and because of the above mentioned experimental data, we have considered an epitaxial cobalt monolayer on the copper substrate. Therefore, in the case of Co—Co (Cu—Cu) bonds we use the Co (Cu) bulk force constants and their geometrical average for Co—Cu bonds. These are the only input parameters of the calculations.

TABLE I. Theoretical and experimental values of $10^3\Delta\sigma^2$ (in angstroms squared); $\Delta\sigma^2=\sigma^2(300\text{ K})-\sigma^2(77\text{ K})$. In the theoretical designation of the bond type, *B* denotes bulk and *S*, surface.

	Theory	Experiment
Co (*B*-*B*), $\Delta\sigma_{\text{Co}}^2$	2.9	3.8 ± 0.3
Cu (*B*-*B*), $\Delta\sigma_{\text{Cu}}^2$	4.7	4.7 ± 0.5
Co/Cu (*S*-*S*), $\Delta\sigma_{\parallel}^2$	3.1	3.9 ± 0.3
Co/Cu (*S*-*B*), $\Delta\sigma_{\perp}^2$	5.4	4.9 ± 0.5

The MSRD σ_j^2 is given as a function of temperature by

$$\sigma_j^2(T)=\frac{\hbar}{m}\int_0^{\omega_{\max}}d\omega\frac{n_r(\omega)}{\omega}\coth\left|\frac{\hbar\omega}{2k_BT}\right|, \tag{3}$$

where ω is the phonon eigenfrequency and m is the mass of a Co (Cu) atom for Co—Co (Cu—Cu) bonds and twice the reduced mass of Co and Cu for Co—Cu bonds. $n_r(\omega)$ is the normalized projected density of modes contributing to the relative vibrational motion. This "two site" density of modes is obtained analytically from the continued-fraction method[15, 17] so that σ_j can be easily calculated in the whole range of temperature.

Results are displayed in Fig. 2(a). For a pair of surface Co atoms the values are intermediate between those for bulk Co and Cu, though obviously much nearer to Co. On the contrary, the value of σ_j for a Co—Cu bond is larger than σ_j^{bulk} even for Cu. Since the Co force constants are larger than the Cu ones, one can wonder if the observed anisotropy is a surface

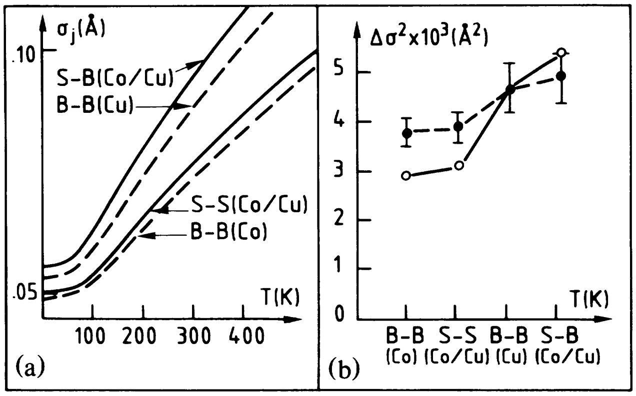

FIG. 2. (a) Square root of the mean square relative displacements as a function of temperature for bulk Co and Cu (dashed lines) and for a surface-surface bond (*S*-*S*) and a surface-bulk bond (*S*-*B*) (solid lines) calculated for a monolayer of Co on Cu (111). (b) Theoretical (open circles) and experimental (filled circles) value of $\Delta\sigma^2=\sigma^2(300\text{ K})-\sigma^2(77\text{ K})$ for the different systems.

effect or a simple bonding effect. It is clear that hypothetical Co-Cu bulk would lead to $\sigma_j(\mathrm{Co}) < \sigma_j(\mathrm{CoCu}) < \sigma_j(\mathrm{Cu})$ and not $\sigma_j(\mathrm{Cu}) < \sigma_j(\mathrm{Co/Cu}, S\text{-}B)$ as is the case. Therefore, this effect is clearly due to the presence of the surface as in the case of clean Cu,[5] and can be understood as follows. Equation (3) shows that σ_j is directly related to $n_r(\omega)$: In fact, whereas the density of states for a bond parallel to the surface is rather similar to the bulk one, it is perturbed for bonds involving surface and bulk atoms. It is due to the existence of surface modes which leads to an increase of the weight of the low-frequency modes. This obviously enhances the value of σ_j for a surface-bulk pair. This effect is analogous to that found for mean square displacements,[14] but the correlation between motions of atoms must be taken into account properly to obtain quantitative values fo the MSRD.

The calculated $\Delta\sigma_j^2 = \sigma_j^2(300\ \mathrm{K}) - \sigma_j^2(77\ \mathrm{K})$ values successfully compare with the experimental data [Table I and Fig. 2(b)]. Let us notice that, since the experiments are performed at temperatures outside of the range of validity of simpler approaches such as Einstein or Debye models, the elaborate calculation is necessary for us to be confident in the numerical results.

We have unambiguously shown a large anisotropy of surface atom displacements on the (1×1) Co/Cu (111) surface by a straightforward analysis of SEXAFS measurements. So care must be taken in the interpretation of polarization-dependent amplitude ratios and low-temperature data are more advisable even to determine geometric parameters. Independent calculations confirm the power of the technique to give quantitative information about the local modes of vibrations. Moreover, the results enhance the confidence in such calculations to describe clean surfaces.

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