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

In a recent paper[1] we have shown that x-ray polarization-dependent surface extended x-ray-absorption fine structure (SEXAFS) permits the measurement of the anisotropy of the mean square relative displacements of the surface atoms in directions parallel and perpendicular to the surface. Results for the epitaxial, unrelaxed, (1×1)Co/Cu(111) surface (simulating a fcc densely packed clean surface) show a larger amplitude in the correlated surface-atom vibrations perpendicular to the surface than in those parallel. The anisotropy in such a system is understood in terms of the additional freedom for atomic motion in the normal direction, and compares well with calculations based on force constants which take into account atomic motion correlations. However, it seems clear to us that surface reconstruction, relaxation, buckling, and other surface phenomena such as chemisorption will imply vibrational anisotropies of other kinds.

In a recent Letter[2] Sette *et al.* present a SEXAFS analysis of the C(2×2)Cl/Cu(100) surface system and conclude that "the 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." By looking at a simple representation of this system in Fig. 1, and by using simple force-constant ideas together with symmetry concepts, one recognizes the directional forces acting on the Cl and Cu atoms. By projecting these forces on the directions parallel and perpendicular to the surface, one finds for $Cl_{\parallel}$

$$2K_{Cl-Cu}\sin^2 49.7 = 1.16K_{Cl-Cu};$$

and for $Cl_{\perp}$

$$4K_{Cl-Cu}\cos^2 49.7 = 1.67K_{Cl-Cu}.$$

Within the harmonic approximation, $\langle u^2\rangle$ is proportional to $1/K$. So the result of a larger mean square amplitude for the Cl parallel to the surface is easily understood, being a natural consequence of the geometry.

The force acting on the Cu surface atoms perpendicular to the surface is, for $Cu_{\perp}$,

$$2K_{Cl-Cu}\cos^2 49.7 + 4K_{Cu-Cu}\sin^2 45 = 0.83K_{Cl-Cu} + 2K_{Cu-Cu}.$$

However, because of the local lower symmetry of the Cu–Cl bonds, an in-plane asymmetry exists for the Cu atoms, with stiff directions parallel to and soft directions perpendicular to the Cl–Cl directions (Fig. 1): for $Cu_{\parallel 1}$,

$$2K_{Cl-Cu}\sin^2 49.7 + 6K_{Cu-Cu}\cos^2 45 = 1.16K_{Cl-Cu} + 3K_{Cu-Cu};$$

for $Cu_{\parallel 2}$, $3K_{Cu-Cu}$. Since $K_{Cl-Cu} > K_{Cu-Cu}$ because of the ionicity of the Cl–Cu bonds,[2] the in-plane asymmetry is very large. For example, by taking[3,4] $K_{Cl-Cu} \simeq 1.5K_{Cu-Cu}$ we obtain

$$\Delta\langle u^2_{Cu\parallel 2}\rangle \simeq 1.08\Delta\langle u^2_{Cu\perp}\rangle, \quad \Delta\langle u^2_{Cu\parallel 2}\rangle \simeq 1.6\Delta\langle u^2_{Cu\parallel 1}\rangle.$$

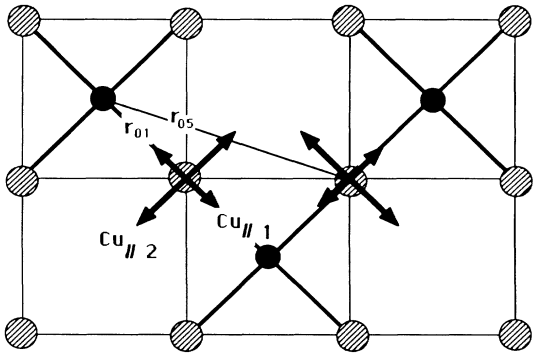

FIG. 1. Top view of the C(2×2)Cl (black atoms) on Cu(100) (hatched atoms). The thick arrows indicate the in-plane Cu-atom vibrational axes.

Sette *et al.* claim that "the Cu surface atoms must follow the Cl surface anisotropy" because of the strong Cl-Cu correlation. The authors assume that correlation is a first-neighbor problem, and project the "uncorrelated relative displacements along r_{05} onto r_{01}" for estimating the correlation term for Cl-Cu motions (cf. Fig. 1, which uses the notations of Ref. 2). There are two mistakes in this procedure: First the Cu in-plane anisotropy effect on the SEXAFS-derived σ^2 values is disregarded. The Cu in-plane vibrations along the soft direction are perpendicular to the Cl–Cu bonds r_{01}, but they have a very large projection along the r_{05} direction. Then the difference between $\Delta\sigma_1^2$ and $\Delta\sigma_5^2$ cannot be attributed only to the correlation term. Second, r_{05} is not a high-symmetry direction and the projection onto r_{01} of the relative displacements of the atoms lying along r_{05} is not a minimum value of $\Delta\langle u_0^2\rangle + \Delta\langle u_1^2\rangle$.

As shown above, Ref. 2 does not give information on the possible asymmetry of the substrate surface vibrations, since the argument used to determine the anisotropy of the vibrations of the copper surface atoms (which is the strongly correlated Cl-Cu motion) is not supported by the data, and the existence of the in-plane Cu asymmetry adds an unknown parameter to the problem.

Dominique Chandesris and Giorgio Rossi
Laboratoire pour l'Utilisation du
Rayonnement Electromagnetique
Université de Paris-Sud
F-91405 Orsay, France

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