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Structure of the $c(2\times 2)$ coverage of Cl on Ag(100): A controversy resolved by surface extended x-ray-absorption fine-structure spectroscopy

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By performing surface extended x-ray-absorption fine-structure measurements, we have resolved the discrepancies between previously reported results for the adsorbate-substrate bond length in Ag(100)$c(2\times 2)$-Cl. The Cl atoms form a simple overlayer occupying the fourfold hollows of the silver surface with a Cl-Ag distance of 2.69 ± 0.03 Å, in agreement with a published low-energy electron diffraction study, though with greater precision.

An accurate knowledge of the bond length and coordination geometry for atoms adsorbed on single-crystal surfaces is the basis for all modern surface science. Several techniques can give these parameters to sufficient accuracy, but to date few adsorption systems have been studied by more than one method, although such a cross check is, of course, highly desirable to increase one's confidence in the reliability of the structural information. Unfortunately, conflicting results were produced by different techniques applied to the half-monolayer $c(2\times 2)$ coverage of Cl on Ag(100). There has been disagreement on whether the data were best described by a simple overlayer model (SOM) or a mixed layer model (MLM), with a quasiepitaxial AgCl surface layer, and there is also dispute on the adsorbate-substrate bond length. We believe we have resolved the discrepancy by our surface extended x-ray-absorption fine structure (SEXAFS) measurements, reported here, which agree with published low-energy electron diffraction (LEED) experiments.[1] The system is fit by a SOM, with the Cl atoms in the fourfold hollows of the Ag(100) surface, at a Cl—Ag bond length of 2.69 ± 0.03 Å.

The Ag(100)$c(2\times 2)$-Cl surface system has been the subject of a considerable number of previous investigations. Early work[2] was reported to be suggestive of a mixed layer model (MLM) with chlorine atoms occupying substitutional positions on the silver surface, like a monolayer of epitaxial AgCl. LEED intensity (*I-V*) analysis[1] also gave a reasonable fit to the MLM, but yielded best agreement with a SOM with Cl in the fourfold hollows of the unreconstructed Ag surface at a Cl—Ag bond length of $2.67^{+0.03}_{-0.10}$ Å, later reanalyzed[3] as 2.64 Å, with the same data subsequently reported[4] to give a best value of 2.61 Å. Further LEED work[5] and helium atom diffraction measurements[6] supported a SOM, although neither was able to derive fully quantitative structural information. Comparisons of the electronic density of states of Ag(100)$c(2\times 2)$-Cl as measured by angle-integrated photoemission[7] and calculated by tight-binding[8] and augmented-plane-wave[9] methods agreed only for the MLM. However, angularly resolved photoemission data[10] contained features consistent only with the calculations[8,9,11] for the SOM. It has been suggested[6] that the atomic smoothness of the Ag surface might be crucial, with rougher areas forming patches of "AgCl;" this could explain the reported surface phase transition[12] which could not be reproduced by other workers.[13] In view of the possible implications for overlayer growth modes,[14] as well as its intrinsic interest, it is important to establish the correct surface structure for the Cl on Ag system.

Surface EXAFS is an ideal technique for determination of adsorbate-substrate bond lengths.[15,16] The x-ray absorption cross section exhibits fine structure (the EXAFS) as a function of photon energy, caused by interference between the emitted photoelectron wave and the waves backscattered from surrounding neighbor atoms. Since the period of the oscillatory structure depends on the photoelectron wave vector and the distance between absorbing and backscattering atoms, SEXAFS is a particularly direct method of deriving near-neighbor bond lengths.

The experiments were carried out on the SEXAFS beamline[17] at the Daresbury Laboratory Synchrotron Radiation Source. The Ag(100) crystal was cleaned by repeated cycles of Ar^+ bombardment and annealing, and its cleanliness and surface order was checked by Auger electron spectroscopy and LEED. Exposure to chlorine from an electrolytic source produced a sharp $c(2\times 2)$ LEED pattern at 0.5-monolayer coverage. The monochromator was scanned from 2800 to 3200 eV, through the Cl K edge at around 2820 eV, and surface EXAFS spectra were recorded in the total electron yield mode by measuring the current collected by a detector placed close to the sample, which was at room temperature. Normalization to the incident photon flux was achieved by monitoring the drain current of a thin (0.75-μm) Al foil placed between the monochromator and the sample. A raw SEXAFS spectrum (measured at room temperature), after removal of a smooth background, conversion to k space, and weighting by k^3 to enhance the weaker oscillations, is depicted in

Fig. 1(a), with the back-transformation of the Fourier-filtered first shell superimposed. This nearest-neighbor oscillation and its Fourier transform are shown as the solid lines in Figs. 1(b) and 1(c). Analysis of the EXAFS data was performed using a curve-fitting routine based on the rapid curved wave method[18] to give the theoretical spectra shown as the dashed lines in Figs. 1(b) and 1(c).

To turn a peak in the Fourier-transform (FT) data into a real distance it is necessary to correct for the scattering phase shifts due to the absorbing (Cl) and backscattering (Ag) atoms. These phase shifts were calculated using a "muffin-tin"-potential-based method, then refined to fit the EXAFS spectrum measured from the AgCl model compound. EXAFS spectra were recorded from a large number of bulk metallic halides, and significant anharmonic effects found in data taken at room temperature.[16] For the purposes of obtaining reliable phase shifts from model compounds, the main result of anharmonicity is to introduce an additional phase-shift correction term.[19] We derived the magnitude of this correction term from analyses of EXAFS spectra of model compounds measured at room temperature and at low temperatures where anharmonic effects were negligible. The surface EXAFS data were then corrected by this extra distance (0.06 Å for Cl-Ag) derived from the temperature-dependent bulk measurements. The validity of this procedure has been verified by making surface EXAFS measurements for Cl on Ag(111) at different temperatures.[20] The result of this analysis is that the Cl-Ag nearest-neighbor distance on Ag(100) is found to be 2.69 ± 0.03 Å; the same, within experimental error, as found for Cl on the Ag(111) surface.[20]

The most frequently used way of determining adsorption sites from SEXAFS is to vary the photon incidence angle and monitor the change in effective coordination number (N_i^*) as the amplitude weighting from the neighbors is changed.[21] However, in this particular experiment it proved impossible, owing to instrumental problems, to perform satisfactory SEXAFS measurements at a grazing angle of incidence. Further, it has recently been demonstrated that there may be significant anisotropy in the vibrational (Debye-Waller-like)[22,23] and surface mean-free-path[23] terms, giving varying amplitude attenuation for atoms in different directions from the adsorbate atom, and thus confusing attempts to derive values of N_i^*. Nevertheless, the measurement at normal incidence alone, for this adsorption system, allows unequivocal distinction between the expected high-symmetry sites. For a nearest-neighbor Cl-Ag distance of 2.69 Å and an unreconstructed Ag(100) surface, the expected values of N_i^* become[15,21] 0 (onefold atop site), 0.9 (twofold bridge site), 3.5 (fourfold hollow site), and 9.5 (MLM). The differences between these figures are so great that they are unlikely to be confused by anisotropic amplitude effects.[22,23] We find $N_i^* = 3.8 \pm 0.5$, using the same (isotropic) mean free path and Debye-Waller-like factors as for Ag(111)-Cl (Ref. 20). This directly indicates the fourfold hollow site in a SOM. We note that the bond-length value is inconsistent with an epitaxial Ag-Cl overlayer with $c(2\times2)$ symmetry, which would require Cl-Ag distances equal to, or greater than, the bulk Ag-Ag value

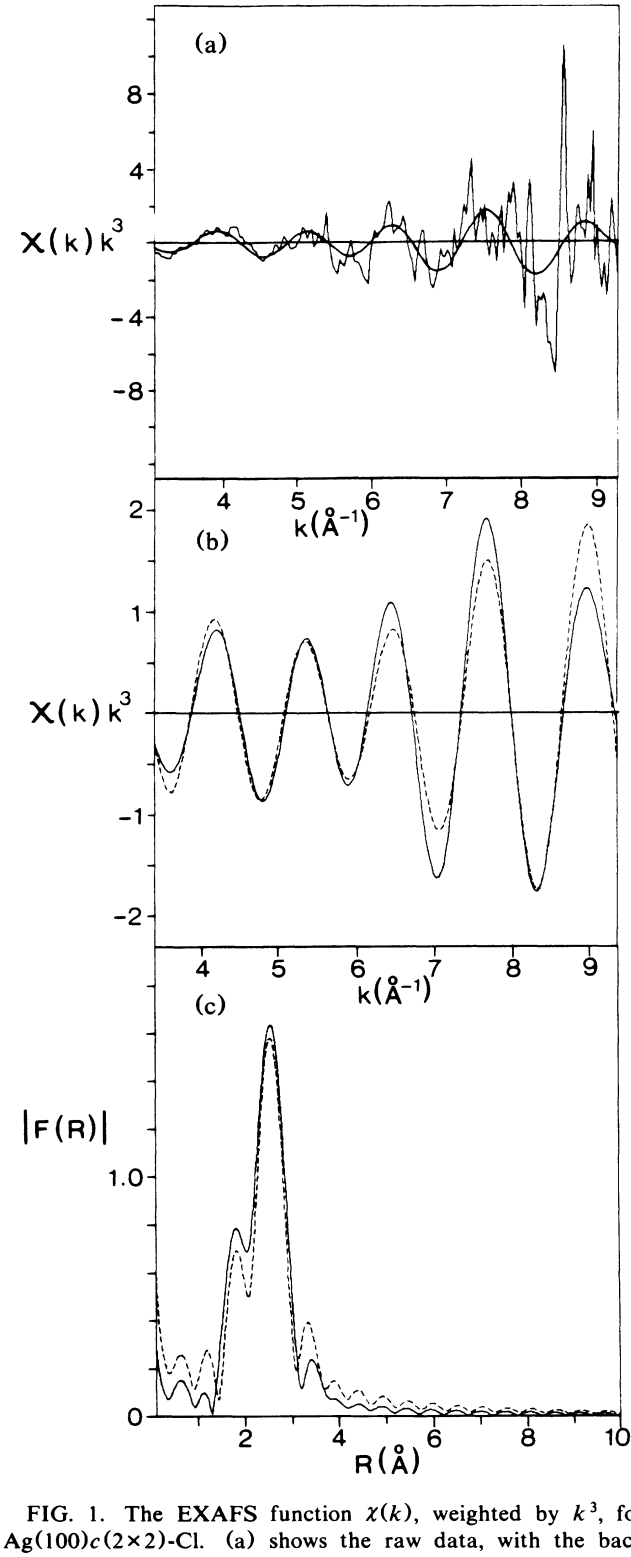

FIG. 1. The EXAFS function $\chi(k)$, weighted by k^3, for Ag(100)$c(2\times2)$-Cl. (a) shows the raw data, with the back transformation of the Fourier-filtered first shell oscillation superimposed. (b) gives this same first shell oscillation, with an expanded ordinate scale, and (c) its Fourier transform, with the experimental data denoted by the solid lines and the theoretical best fit given by the dashed lines. The abscissa in (c) gives the real distance, after correction for the Cl-Ag phase shift.

(2.88 Å), depending on the relative vertical spacing of the top-layer Cl and Ag atoms. Thus our bond-length determination alone completely rules out a MLM.

Suggestions for the structure of the Ag(100)$c(2\times2)$-Cl system have previously been made by considering the analogous system of $c(2\times2)$ Cl on the (100) face of copper. A LEED I-V study[24] found Cl to sit in the fourfold hollows at a bond length of 2.38 Å, and surface EXAFS measurements[25] were in excellent agreement, with a Cl-Cu distance of 2.37 ± 0.02 Å. These authors were unable to obtain good quality SEXAFS data for the Cl on silver system, and attempted to deduce a Cl-Ag distance from their result for Cl-Cu. They defined a "surface radius" of 1.09 Å for Cl by subtracting the Cu metallic radius[26] (1.28 Å) from the Cu—Cl bond length. Adding this to the metallic radius of Ag (1.44 Å) they[25] suggest a surface Cl-Ag distance of 2.53 Å. This work was claimed to "resolve previously reported discrepancies for the Ag(100)$c(2\times2)$-Cl system,"[25] but unfortunately it only added to the confusion with this incorrect deduction of a Cl—Ag bond length which proves to be as much as 0.16 Å shorter than the actual value, reported here.

It is interesting to consider the reason for failure in this attempt to transfer effective radii for Cl on Cu to Cl on Ag. We note that it has long been recognized that chemical bonds involving silver are awkward to fit into any empirical scheme for interatomic radii both in bulk crystals[27] and at surfaces.[28] The distance suggested above[25] would be for a covalent Cl-Ag surface bond: It is known that most silver compounds are more ionic than the equivalent copper ones, and so it is not surprising that a larger Cl radius on the Ag surface is indicated.

In summary, we have studied the Ag(100)$c(2\times2)$-Cl system with surface EXAFS, and find the Cl atoms form a simple ovelayer, occupying the fourfold hollows with a Cl-Ag distance of 2.69 ± 0.03 Å, in agreement with a previous LEED study and contradicting other suggested surface structures and bond lengths.

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