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Surface structural determination for a weakly ordered and a disordered phase of Cl on Ag(111)

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Surface extended x-ray-absorption fine-structure measurements have been made for the structure of two weakly ordered phases of chlorine adsorbed on Ag(111) at coverages of one-third and two-thirds of a monolayer. The Cl atoms are found to occupy threefold hollows on the silver surface, at a Cl-Ag distance of 2.70 ± 0.01 Å, independent of coverage. A full multishell fit, including neighbor shells as far as about 5.2 Å, allows a complete structural determination: At $\frac{2}{3}$ monolayers the Cl forms a vacancy honeycomb structure, while at the lower coverage Cl-Cl nearest-neighbor sites are avoided.

The adsorption of chlorine onto low-index faces of silver is one of the most studied systems in modern surface science. Despite this effort, however, there is a lack of good quantitative information on adsorbate-substrate bond lengths and coordination sites for Cl on Ag(111). This is largely because the submonolayer structures form without long-range order, which is an essential prerequisite for study by low-energy electron diffraction (LEED)[1] or other diffraction techniques. In this respect surface extended x-ray-absorption fine-structure (SEXAFS) measurements hold a major advantage, since the technique probes only the *local* structure around adsorbate atoms, and is thus the technique of choice for studying disordered surface phases. This paper reports the results of a SEXAFS study of both a disordered and a weakly ordered phase of Cl on Ag(111). Analysis of the data with a multishell curve-fitting procedure, as far as we know not previously reported for a surface EXAFS study, allows a precise determination of several neighbor distances, and we derive models for the adsorbate structures formed.

The experiments were performed using the SEXAFS facility at the Daresbury Laboratory synchrotron radiation source.[2] The silver crystal was cleaned by the usual methods of argon-ion bombardment and anneal cycles until no contamination was visible in Auger electron spectra (AES) and the surface exhibited a sharp (1×1) LEED pattern. The crystal was dosed at room temperature with chlorine from an electrolytic source, with Cl coverages monitored by AES and checked by the magnitude of the Cl x-ray-absorption signal. As chlorine was adsorbed on Ag(111) no LEED pattern was formed until a coverage of about two-thirds of a monolayer (ML) (defined in terms of the numbers of Ag surface atoms), when a very weak and diffuse $(\sqrt{3}\times\sqrt{3})R30°$ structure was seen. This observation agrees with previous reports.[3-5] Surface EXAFS spectra were measured above the Cl K edge at around 2820 eV, and the absorption coefficient was monitored in the total-electron-yield mode by recording the current collected by a detector placed close to the sample. This system cannot be studied by using the Cl *KLL* Auger electron yield, because of the overlap with photoelectron peaks from Ag M levels. Normalization to the incident photon flux was achieved by monitoring the drain current of a thin Al foil placed between the monochromator and the sample. All of the spectra presented here were recorded with the photon beam incident along the sample normal. Figure 1 shows a raw SEXAFS spectrum of the $\frac{2}{3}$-ML coverage of Cl on Ag(111), measured at $T = 100$ K.

The data were analyzed, after the usual background subtraction and conversion to k space, by a curve-fitting routine based on the rapid curved-wave computational scheme.[6] Electron scattering phase shifts for Cl and Ag were calculated using a "muffin-tin"-potential-based method, then refined to fit our measured EXAFS spectrum from AgCl. The separate empirical absorber and backscatterer phase shifts were transferred in a variety of combinations to a large number of bulk compounds with a

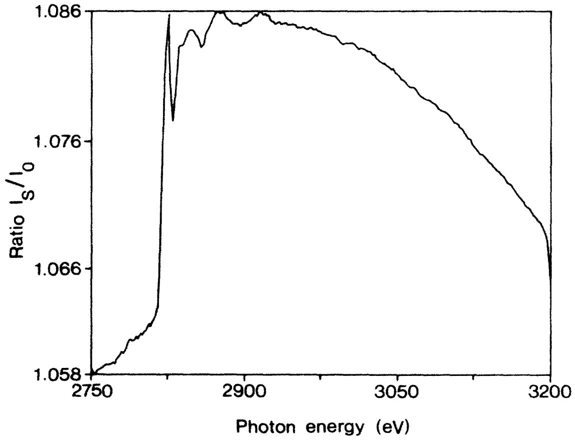

FIG. 1. A raw SEXAFS spectrum for $\frac{2}{3}$ ML of Cl on Ag(111), measured at $T = 100$ K. The dip at the end of the spectrum (3200 eV) is caused by increased absorption at the K edge of Ar, present as a contaminant in the incident flux monitor.

common atom, and our Cl and Ag phase shifts were found to be almost perfectly interchangeable, incurring an inaccuracy in bond distances of less than 0.01 Å. EXAFS spectra were recorded from a large number of bulk metallic halides, and significant anharmonic effects found in data taken at room temperature. These findings are discussed in detail elsewhere,[7,8] but we note that, for the purposes of obtaining reliable phase shifts from model compounds, the main effect of anharmonicity is to introduce an additional phase shift[9] to the normal term involving the photoelectron emission from the absorbing atom and its backscattering from a neighbor. The magnitude of this additional phase shift can be derived from an analysis of EXAFS spectra of model compounds measured at room temperature and at low temperatures where anharmonic effects are insignificant. Neglect of anharmonic effects would lead to the change in nearest-neighbor Ag-Cl distance in AgCl between 100 and 290 K appearing to be −0.06 Å, compared to the known thermal expansion of +0.015 Å.

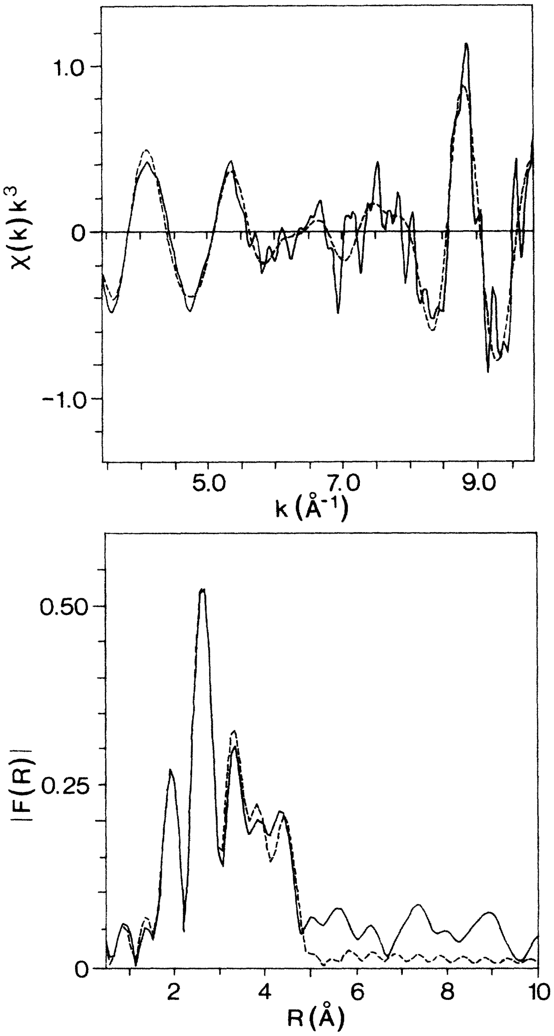

FIG. 2. The EXAFS function $\chi(k)$, weighted by k^3, and the absolute value of the Fourier transform of the SEXAFS data for $\frac{2}{3}$ ML of Cl on Ag(111) (solid lines), compared to the theoretical best fit (dashed lines) using the multishell least-squares curve-fitting method. The abscissa gives distances without phase shift correction. The apparent peak at ~2 Å is produced by a Ramsauer-Townsend resonance in the Ag backscattering amplitude.

All of our bulk and surface EXAFS measurements were performed at $T = 100$ and $T = 290$ K. It is interesting that the temperature-induced apparent change in Cl-Ag distance was the same, within experimental error of ±0.01 Å, for both bulk AgCl and for Cl adsorbed on Ag(111). This suggests that the form of the Cl-Ag interatomic pair potential at the surface is not significantly different from in the bulk.

The results of this curve-fitting analysis for the $\frac{2}{3}$-ML phase of Cl on Ag(111) are given in Fig. 2, which shows (solid line) the experimentally derived spectrum, after background subtraction and conversion into wave-vector space, and (dashed line) the best theoretical fit to the data, together with the corresponding Fourier transforms. This is a full multishell calculation: The nearest-neighbor Cl-Ag and Cl-Cl distances are sufficiently close to each other that the method of Fourier filtering and windowing peaks due to individual shells, used in all previous SEXAFS analyses,[10] cannot work for this overlayer system. The data allow derivation of distance for the first four neighbor shells (two Cl-Ag and two Cl-Cl), which strongly suggest the surface structure depicted in Fig. 3. This is a simple overlayer model, having the correct symmetry for the observed LEED pattern, with Cl atoms postulated to occupy two-thirds of the "fcc" threefold hollows of the silver surface at a Cl-Ag nearest-neighbor distance of 2.70 ± 0.01 Å. No other surface structure with a $(\sqrt{3}\times\sqrt{3})R30°$ unit mesh produced even a reasonable fit to the data, and the "mixed-layer model," a quasiepitaxial AgCl monolayer, suggested previously,[3] is completely ruled out. The distances derived from SEXAFS and those corresponding to the honeycomb structure are given in Table I, where it is seen that agreement with this model is good. We emphasize that these distances come directly from the experimental data and that this model is *not* an input to the theoretical calculation. This is in contrast to LEED inten-

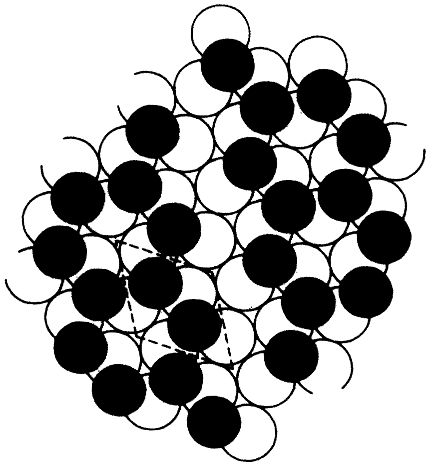

FIG. 3. The vacancy honeycomb structure proposed for the $\frac{2}{3}$-ML coverage of Cl on Ag(111). Two domains are shown, and the unit mesh is outlined.

TABLE I. A comparison of experimental and theoretical real-space components in the $(\sqrt{3}\times\sqrt{3})R30°$ structure observed when $\frac{2}{3}$ ML of chlorine are adsorbed on Ag(111).

	Shell	Model bond distance R_i (Å)	Experimental bond distance R_i (Å)
1.	Cl-Ag	2.70	2.70 ± 0.01
2.	Cl-Cl	2.89	2.93 ± 0.03
3.	Cl-Ag	3.95	3.71 ± 0.10
4.	Cl-Cl	5.00	4.83 ± 0.15

sity analysis, where trial structures have to be assumed and calculations performed for each model. Note that this structure could not be determined from LEED *I-V* analysis as the LEED spots are too weak and diffuse. With domains of the depicted honeycomb structure, LEED would be dominated by antiphase domain scattering, but SEXAFS samples only the strong local order. The overlayer structure depicted in Fig. 3 represents the first full multishell determination for a submonolayer surface system by SEXAFS.

A similar multishell analysis was performed for the $\frac{1}{3}$-ML coverage, for which the LEED pattern showed just the substrate (1×1) symmetry with diffuse scattering superimposed, thus indicating a disordered overlayer. The best fit is shown in Fig. 4, with distances tabulated in Table II. Comparing the analysis of the $\frac{1}{3}$-ML structure with the $\frac{2}{3}$-ML phase, we observe the *complete absence of the first* Cl *shell* at 2.90 Å at the lower coverage. The remaining shells are present and located at the same spacing for the two coverages. It is concluded that the $\frac{1}{3}$-ML structure is also a simple overlayer, with Cl atoms again in the threefold hollow sites, but with avoidance of the nearest-neighbor Cl sites depicted as filled in Fig. 3. Since no new LEED pattern is observed, the Cl adatoms form a disordered overlayer at this coverage; presumably the Cl-Cl next-nearest-neighbor interactions are weaker than the Cl-Cl nearest-neighbor interactions, which dominate in the formation of the $\frac{2}{3}$-ML structure, and the $(\sqrt{3}\times\sqrt{3})R30°$ "domains" are much smaller at $\frac{1}{3}$ ML than the coherence width of the LEED electron beam.

The Cl-Ag nearest-neighbor distance is obtained as 2.70 Å in both cases, shorter than the value of 2.77 Å in bulk AgCl, with comparison between different sets of experimental data showing the *first shell* spacing to be reproducible to better than 0.01 Å (higher shells have considerably larger error bars). It might have been anticipated that the proximity of three neighboring Cl atoms in the $\frac{2}{3}$-ML structure would provide a sufficiently repulsive interaction to cause a measurable increase in adsorbate-substrate bond length. Although an independence of bond length on coverage has been reported for other systems, for instance, the $p(2\times2)$ and $c(2\times2)$ phases of the chalcogens on Ni(100) (Ref. 11), the present work is the first time that bond lengths have been measured for a simple overlayer system at different coverages with anything approaching 0.01-Å accuracy.

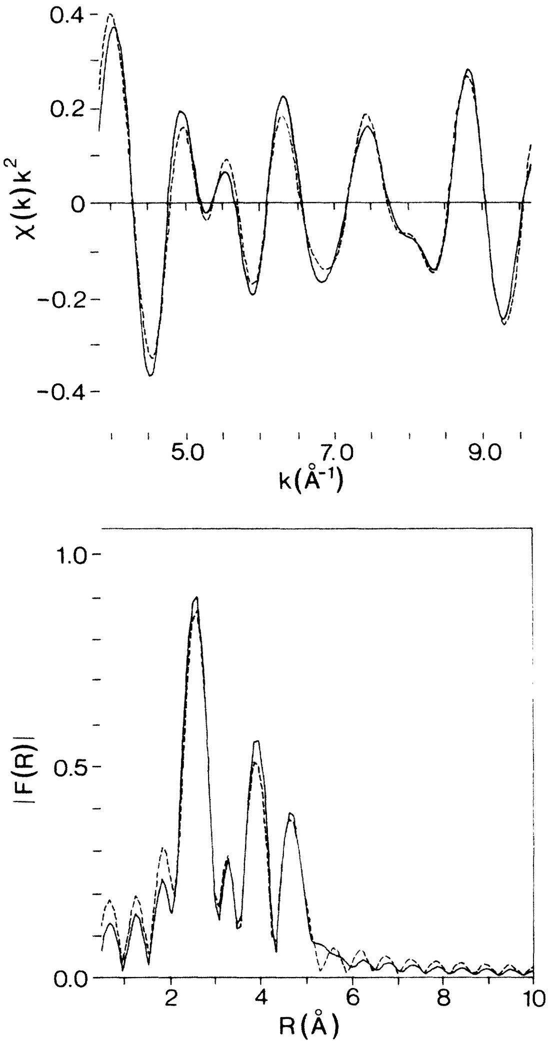

FIG. 4. The EXAFS function $\chi(k)$, weighted by k^2, and the absolute value of the Fourier transform of the SEXAFS data for $\frac{1}{3}$ ML of Cl on Ag(111) (solid lines), compared with the best theoretical fit (dashed lines). For this coverage only, noise corresponding to real-space components >5.2 Å has been filtered from the raw data.

TABLE II. A comparison of experimental and theoretical real-space components in the phase formed when $\frac{1}{3}$ ML of chlorine are adsorbed on Ag(111). The close-packed Cl-Cl component observed in the $\frac{2}{3}$ ML structure is absent in this lower coverage phase but the first nearest-neighbor Cl-Ag distance is the same in both high and low coverage cases.

	Shell	Model bond distance R_i (Å)	Experimental bond distance R_i (Å)
1.	Cl-Ag	2.70	2.70 ± 0.02
2.	Cl-Ag	3.95	3.68 ± 0.06
3.	Cl-Cl	5.00	5.14 ± 0.20

In summary, SEXAFS has enabled a precise structural determination for the adsorption of Cl on Ag(111) at coverages up to two-thirds of a monolayer. The adatoms are adsorbed into threefold hollow conventional substrate sites; repulsive interactions between Cl atoms result in spreading of the overlayer, with exclusion of nearest-neighbor sites at coverages up to $\frac{1}{3}$ monolayers. The $\frac{2}{3}$ monolayer, with a weakly ordered $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure, is a vacancy honeycomb (or graphitic) simple overlayer. The Cl-Ag bond length is 2.70 ± 0.01 Å, independent of coverage between $\frac{1}{3}$ and $\frac{2}{3}$ monolayers.

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