Determination of an Adlayer Bonding Transition by Surface Extended X-Ray-Absorption Fine-Structure Spectroscopy: Cesium Adsorbed on Ag{111}

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As the Cs coverage of Ag{111} is increased from approximately 0.15 to 0.3 monolayer the Cs-Ag bond length is found to increase from 3.20 ± 0.03 to 3.50 ± 0.03 Å. This dramatic change is associated with a transition in the cesium bonding from predominantly ionic at low coverage towards a more covalent state at high coverage.

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The potential provided by surface extended x-ray-absorption fine structure (EXAFS) for accurate bond-length determination[1] is exploited in the present work in an effort to provide some insight into the coverage dependence of the bonding mode of alkali metals on metal surfaces. Recent theoretical work on the coverage dependence of the work function of metals upon alkali-metal adsorption[2-4] emphasizes the need for a proper experimental evaluation of the adsorbate-substrate bond length.

Adsorption of alkali-metal atoms onto a metal surface results in a substantial decrease in the work function as the surface charge distribution becomes dominated by the electropositive atoms.[5] As saturation of the first layer is reached, the work function approaches that of the close-packed surface of the alkali metal itself. These results, together with recent plasmon dispersion measurements,[6] are interpreted as indicating that the alkali atoms change continuously from the ionic state towards their neutral (metallic) state[7] as the alkali-metal coverage is increased, in the submonolayer range. We note that it has alternatively been suggested that the adsorption of Cs on W, Mo, and Ta is covalent at *all* coverages[8]; the photoemission results of Hohlfield, Sunjic, and Horn,[9] however, for Cs on Al{111}, strongly support an ionic model at low coverages. Since the effective radius of an atom depends on its charge state, any change in ionicity should be accompanied by a change in adsorbate-substrate bond length.

Surface EXAFS is an ideal technique for the determination of bond-length changes in overlayers, since it probes directly the structural environment around an adsorbate atom, and does not rely on long-range order. The technique has been extensively reviewed elsewhere,[10-12] so that here we merely summarize the salient points for this particular application. EXAFS refers to the part of an absorption spectrum above a core ionization level which shows oscillatory structure as a function of photon energy: This structure in the absorption coefficient is caused by interference between the emitted photoelectron wave and the waves backscattered from surrounding neighbor atoms. Thus the EXAFS exhibits an amplitude and phase determined by the spatial distribution and electron scattering properties of the absorber atom and its near neighbors. The details of the amplitude terms do not concern us in this present discussion, and so we may express the EXAFS functions of $\chi(k)$ as a function of photoelectron wave vector k, in the form

$$\chi(k)=\sum\{A_d\sin(2kR_i+\Phi_d)+A_s\sin(2kR_i+\Phi_s)+A_{sd}\sin(2kR_i+\Phi_{sd})\}, \quad (1)$$

where the summation i is over near neighbors of the absorber at a distance R_i, A is the amplitude, and Φ is the phase shift suffered by the photoelectron wave on its emission from the absorber and scattering from the neighbor atoms. The suffixes d, s, and sd refer to the angular momentum components allowed by the dipole selection rules for absorption at an $L_3(2P_{3/2})$ edge, with the sd cross term corresponding to emission of an s wave and backscattering of a d wave or vice versa. It is clear that the key to accurate bond-distance determination is the knowledge of accurate phase shifts Φ, and we return to this point later.

Surface EXAFS measurements were performed by our monitoring the total electron yield as a function of photon energy above the Cs L_3 absorption edge of 5012 eV. The surface EXAFS beam line[13] at the Daresbury Laboratory's Synchrotron Radiation Source (SRS) provided about 5×10^{11} photons per second with the SRS running at 1.9 GeV, 200 mA, and using Ge{111} monochromator crystals. The Ag{111} crystal was cleaned by repeated cycles of argon-ion bombardment and annealing, with surface order and cleanliness checked by LEED and Auger-electron spectroscopy. Cesium was evaporated onto the surface at room temperature from a commercially available source, and the coverage monitored from the Cs-Ag Auger peak-height ratio. The close-packed first-layer coverage was determined by saturation dosing at room temperature. Relative coverages were checked from the absorption jump at the Cs edge, which is proportional to the number density of absorbing Cs atoms. All surface EXAFS (SEXAFS) measurements are performed at $T=120$ K to reduce the large Debye-Waller-type damping of the SEXAFS amplitude, which smeared out the oscillations at room temperature. Further, we have previously[10] found this low temperature to be necessary to avoid anharmonic effects in the SEXAFS pair correlation function, and thus an incorrect derivation of interatomic distance. The total background pressure during SEXAFS measurements was 5×10^{-11} mbar, and typical data collection times were 20 min. The apparatus is described elsewhere.[10]

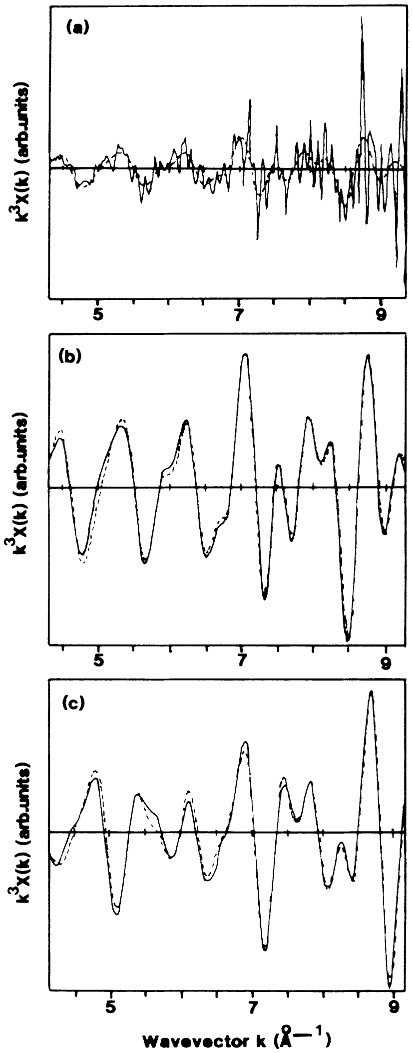

FIG. 1. Background-subtracted experimental SEXAFS spectra $\chi(k)$, weighted by k^3 (full line) with the multishell theoretically calculated best fit (dashed curve) for (a) 0.3 ML of Cs adsorbed on Ag{111} (raw data); (b) the same data after Fourier filtering (note the change in scale of the ordinate axis); and (c) 0.15 ML of Cs adsorbed on Ag{111} (Fourier-filtered data).

Our SEXAFS results are depicted in Fig. 1. Figure 1(a) shows the background-subtracted raw data for 0.3 monolayer (ML) (corresponding to a close-packed layer of Cs on Ag{111}) of Cs with a multishell theoretically calculated curve. A comparison between the Fourier-filtered experimental data and the theoretical calculation is shown in Fig. 1(b). Figure 1(c) displays a similar comparison for a set of data from the 0.15-ML surface. The success of the Fourier-filtering process in the extraction of signal from noise is illustrated by the reproducibility achieved between independent runs: Bond-length variations for both the first and second shells were within ±0.02 Å. There are clearly several frequency components reproducibility present in the data, providing the basis for a multishell analysis.[14] However, in this Letter we are concerned only with presenting nearest-neighbor (nn) shell distances. The bond-length change to the nn Ag shell between 0.15 and 0.3 ML of Cs is illustrated in Fig. 2, where the first nn components from the multishell theoretical curves are extracted and overlaid on the same momentum scale. There is clearly a substantial coverage-dependent frequency change, indicating a large change in bond length. This is the main message of this work.

We consider that Cs-Ag distances are implied by the data in Fig. 1, and assess the confidence limits on this bond determination. Analysis was performed with a least-squares curve fitting method using a rapid curved-wave calculation[15] based on the original theory of Lee and Pendry.[16] Phase shifts and distances are input to the program (along with other structural and nonstructural parameters which do not affect the *bond-length* derivation) and an iteration performed to achieve the best fit to experimental data. In this work we have calculated phase shifts and then empirically modified them to give

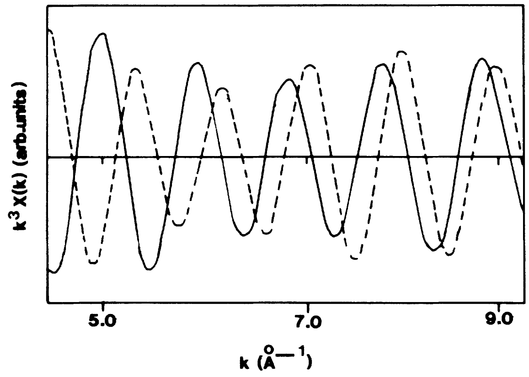

FIG. 2. The frequency component corresponding to the nearest-neighbor Cs-Ag distance for 0.15 ML (full line) and 0.3 ML (dashed line) of Cs on Ag{111}.

the best possible multishell fit to EXAFS spectra of appropriate bulk model compounds. The calculations start with atomic charge densities, computed self-consistently with relativistic corrections, and then superpose these in a muffin-tin form. In this way phase shifts were calculated for Cs and Ag and refined by our fitting EXAFS spectra from the L_3 edges of Cs in CsBr and Ag in AgCl. Transferability of phase shifts was carefully checked against CsCl, AgBr, and Ag metal. This analysis yields only the Φ_d phase shifts in Eq. (1), since A_{sd} vanishes by angular averaging in bulk samples, and A_s is assumed to be small compared to A_d.

With great care and in favorable circumstances,[10] SEXAFS measurements can yield a total accuracy of 0.01 Å. In the experiments reported here, the size of the error bars on the nn bond lengths arising from random statistical error, due to the finite range of the data and the slight differences between successive measurements, is estimated to be ±0.02 Å. However, there are several systematic sources of error which further limit the total accuracy of distance determination in this Cs-Ag system. First, the atomic backscattering factor for Ag contains a Ramsauer-Townsend resonance, the effect of which is to produce a modulation of the SEXAFS amplitude as a function of wave vector. This then gives an additional frequency component corresponding to an apparent peak at a shorter distance. In this Cs-Ag system the "split-off" peak due to the Ag backscattering resonance in the *second* nearest-neighbor Ag shell actually occurs at a distance similar to that of the main peak for the first nn Ag shell. This is not particularly difficult to deal with in our multishell fitting procedure, and will be discussed in more detail elsewhere.[14] Second, we have neglected the *s-d* interference term [Eq. (1)]. This has been suggested[17] to lead to a possible inaccuracy, in the worst case, of 0.04 Å, although normally the bond-length determination should be little affected.[18] The accuracy in the absolute bond length, arising from both random and systematic errors, is thus estimated to be ±0.03 Å; but the accuracy in bond-length change with coverage, which is insensitive to systematic errors, is estimated to be ±0.04 Å.

We find the nearest-neighbor Cs-Ag distance to be 3.20±0.03 Å at 0.15 ML of Cs, and 3.50±0.03 Å for the higher coverage (0.3 ML of Cs); the bond-length increase between these two coverages is 0.30±0.04 Å.

The fractional Cs coverage of 0.3 approximates a close-packed layer. For alkali-metal adsorbates studied on a range of single-crystal substrates, the work function of the close-packed layer corresponds closely to that for the most densely packed plane of the bulk alkali metal.[19,20] Thus, while initial adsorption involves charge transfer to the substrate, increased coverage appears to result in a redistribution of charge with the alkali metal approaching its metallic, zero-valent state. We can obtain some indication of the degree of effective charge transfer at the two coverages for which SEXAFS spectra were measured in the present work by considering the Pauling radii[21] for Cs and Ag: The sums of the radii for metallic Ag (1.44 Å) and the ionic, covalent, and metallic radii for Cs are 3.13, 3.79, and 4.06 Å, respectively. If we assume that it is valid to use the metallic radius for Ag, the lower coverage reported here thus gives a Cs radius within 0.1 Å of its fully ionic value, while the higher coverages gives a radius closer to its covalent value.

A rigorous theoretical treatment of the electronic and structural properties of alkali-metal adsorbates is complex and a full quantitative understanding has not yet been reached. Lang and Williams,[22] using a density-functional approximation, compared the ionic adsorption of Li and Cl with the predominately covalent adsorption of Si, at infinite dilution. Their electronic density contours for Li adsorption show charge buildup between metal and adatom, but they conclude that this is due to the screening of Li^+, with an almost empty Li 2*s* resonance. Recently, the first all-electron, self-consistent calculation[23] for the adsorption of a $c(2\times2)$ structure of Cs on W{001} has shown only small "charge transfer" from Cs to W at this higher coverage. Again, there is a buildup of charge density between the atoms, as in a covalent bond, which is here attributed to polarization of the Cs layer. Our observations are therefore in close accord with theoretical calculations.

The work reported here is, to our knowledge, the first observation of a change in adsorbate-substrate bond length as a function of coverage. Other systems have shown no variation in distance, and our own high-precision SEXAFS study of Cl adsorption on Ag{111} and on Ag{110} gave a Cl-Ag distance that was constant, within experimental error of 0.01 Å, at two different coverages.[24,25] Dipole-dipole repulsions still occur for increasing density of Cl adatoms, but the interatomic distance is unchanged. The differences between electronegative adsorbates and the alkali metals may be explained by the energy of the adsorbate resonance.[22] The Cl 3*p* resonance lies in the filled part of the metal-substrate valence band, well below the Fermi level, and it remains so whatever the coverage of Cl; electron transfer to chlorine will thus always be complete on this model. In fact, the Cl-Ag bond length indicates that bonding is predominantly covalent. The 2*s* resonance of Li (analogous to the 6*s* resonance of Cs), however, is almost empty at very low coverages, lying mainly above the Fermi level; increased occupancy of this resonance as the coverage is increased provides a mechanism for reduction of dipole-dipole repulsion in the adlayer.

In summary, we have used SEXAFS to determine the change in nearest-neighbor bond length for 0.15 and 0.3 monolayer of Cs adsorbed on Ag{111}. This difference is found to be 0.3±0.04 Å, which we attribute to a change from a largely ionic towards a more covalent state in the Cs overlayer.

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