Homogeneous Intermediate Valence of Sm on Cu(001)

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Ordered overlayers of Sm on Cu(001) were studied by low-energy diffraction and x-ray photoelectron spectroscopy. The Sm valence varied linearly from 2 to 2.7 during the formation of the monolayer. We argue that the intermediate valence was homogeneous. The behavior is compared with that of Sm overlayers on Al(001).

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Mixed valence in bulk Sm metal, as observed in photoemission experiments, has been attributed to the presence of divalent surface atoms on an otherwise trivalent material.[1-6] Almost all photoemission studies with Sm have been made on conventional evaporated thin films, and, lacking information to the contrary, presumably in the as-deposited unannealed state. Mason *et al.*[7] studied a series of Sm films on amorphous graphite and found that at low coverages ($\sim 10^{15}$ cm^{-2}) the 2+ state was dominant. The amount of Sm 2+ decreased with increasing coverage, eventually attaining the proportion associated with conventional thin films of Sm. At very low coverages the Sm was shown to arise as clusters with diameters in the range 30 ± 10 Å. Even so the structure of these clusters remained undetermined.

Our approach has been to attempt the preparation of structurally ordered overlayers of Sm on well defined single-crystal substrates and to study them using low-energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). In this manner we have observed three different ordered structural arrangements of Sm on Al(001) in all of which the Sm atom had an average valence 2.95[8,9]; if the residual 2+ contribution were attributed to a final-state shakedown effect, then we concluded that the Sm was trivalent. On the other hand, structural disorder was shown to favor the occurrence of the 2+ state.

In this report we describe similar studies of Sm overlayers on Cu(001) substrate and show that the behavior is different from that observed with Al(001). The experimental technique was similar to that described earlier.[9] In contrast to the case of Al(001), the Sm formed ordered overlayers when the Cu substrate was at room tempreature, but it was advantageous to observe and photograph the LEED patterns with the sample at as low a temperature as possible. The substrate was therefore indirectly cooled with liquid N_2 and heated electrically during evaporation. The vacuum in the specimen chamber was $\leq 3\times 10^{-10}$ mbar and the evaporation process caused only a momentary increase to $\sim 2\times 10^{-9}$ mbar. The XPS data were restricted to the $3d^{5/2}$ lines and counting times were usually 615 s. We were very aware of the importance of avoiding contamination by oxygen, which produces a spurious 3+ concentration, and every effort was made to obtain data for clean Sm overlayers.

We observed two ordered monolayer structures. The first to develop was a square net with side $\sqrt{5}a$, where a is the parameter of the Cu(001) surface net, 2.56 Å. There were two possible orientations of this $\sqrt{5}\times\sqrt{5}$ square net at $\pm 26.57°$ with regard to an axis of the Cu(001) surface layer. Since both orientations arose with equal probability a domain structure formed. In a given domain the Sm sites were crystallographically equivalent with a nearest-neighbor separation of 5.72 Å. The $\sqrt{5}\times\sqrt{5}$ net, in perfect form, produced a coverage, θ, of 0.2 ($\theta = 1$ corresponding to one Sm atom for every surface Cu atom) or a concentration of 3.1×10^{14} cm^{-2}.

When a larger amount of Sm was deposited a hexagonal overlayer arose. The LEED pattern, which occurred together with that of the substrate, showed that the overlayer was a coincidence structure similar to that formed on Al(001), but with the difference that there was no distortion of the hexagonal symmetry with the Cu(001) substrate. Here again there were two possible orientations leading to a quasi-twelvefold symmetrical LEED pattern. This hexagonal layer was complete at a coverage $\theta = 0.381$ and produced a nearest-neighbor separation of 4.48 Å; with regard to the underlying Cu surface layer the Sm atoms occupied six inequivalent sites, although three of these were closely similar. We did not observe the formation of a $\sqrt{2}\times\sqrt{2}$ overlayer and for thicker films no LEED pattern was seen.

Typical spectra for four different coverages of Sm are shown in Fig. 1, whereas in Fig. 2 we have collected data from a series of measurements and plotted the average valence of the Sm atom, as deter-

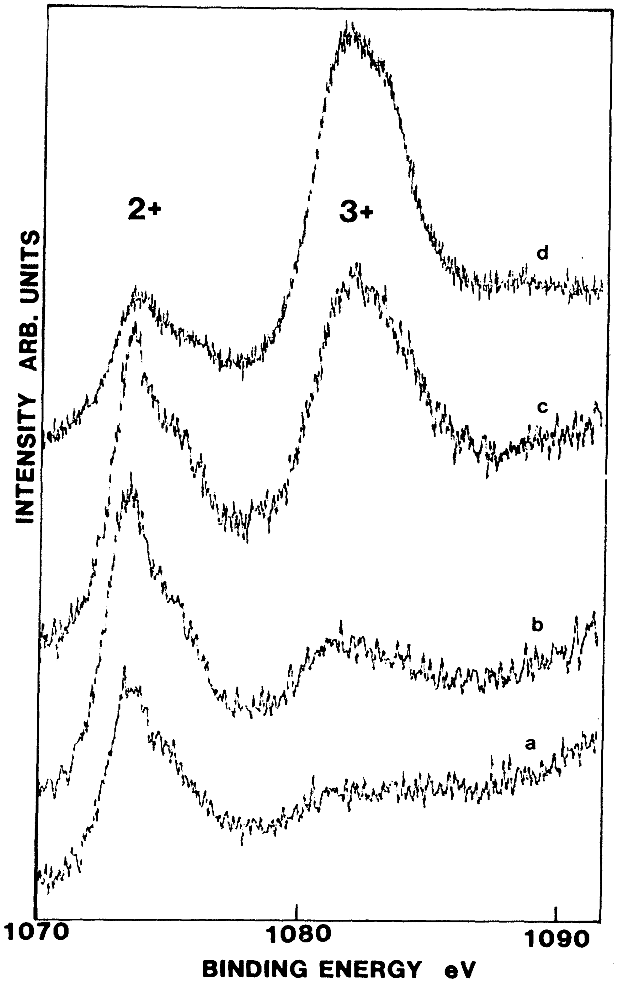

FIG. 1. The x-ray photoemission spectrum of the $3d^{5/2}$ lines for different overlayer coverages of Sm on Cu(001) taken with Al $K\alpha$ radiation. The coverages, estimated with the aid of Fig. 2, are, spectrum *a*, 0.08; *b*, 0.15; *c*, 0.21; *d*, > 0.5. The rising background at high binding energy is due to the proximity of the Cu 2*s* line. Spectrum *d* has an intensity scale factor of $\frac{1}{4}$ relative to the other spectra.

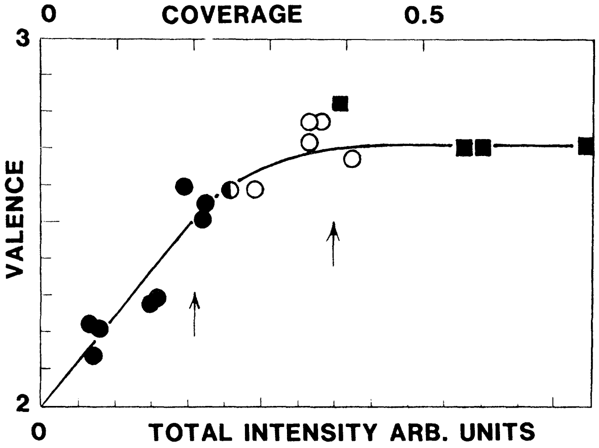

FIG. 2. The average valence as a function of the total $3d^{5/2}$ signal strength. The symbols have the following significance: solid circles, overlayer with $\sqrt{5}\times\sqrt{5}$ structure; open circles, overlayer with hexagonal structure; squares, thicker overlayer for which no LEED pattern was seen. The arrows indicate the positions where the two overlayer structures are completed. It must be remembered that the abscissa has a linear scale only for coverages < 0.5.

mined from the areas of the two components relative to the $3d^{5/2}$ line as a function of the normalized combined area; the latter quantity is used as a measure of the amount of Sm deposited, a procedure which should be accurate for $\theta < 0.5$. In Fig. 2 different symbols indicate the overlayer structures detected by LEED. The data show in clear fashion that the isolated Sm atom on a Cu(001) surface was divalent. The development of the $\sqrt{5}\times\sqrt{5}$ square net led to an increase in the average valence, an increase which continued when this layer progressed to the hexagonal form. Thereafter the average valence maintained a constant value close to 2.7. Using LEED observations we assessed the valence in the complete square net to be 2.5 and that for the hexagonal overlayer to be 2.7. In this way we obtained a quantitative measure of coverage in the range $0 \leqslant \theta \leqslant 0.5$.

For Sm on Cu(001) structural disorder produced by evaporation onto a cold substrate had no pronounced effect on the valence, but in earlier experiments[8] with Sm on Al(001) we found that disorder overlayers favored the occurrrence of Sm 2+, the more so the smaller the coverage. Crystallographic ordering invariably caused a change to the 3+ condition at all coverages studied. It appears that there is a significant difference between the behavior of Sm on the two substrates. However, although certain differences remain, we show that the behavior is probably more similar than it seems at first sight. For very low coverages of Sm on Al(001) a streaking of the LEED pattern was always seen before well developed overlayer diffraction spots arose, but streaking was never seen for Sm on Cu(001). Instead the diffraction spots were initially very diffuse and round, but sharpened as the coverage became optimal. This implies that the Sm atoms on Cu(001) were always uniformly distributed over the substrate. In the fully formed $\sqrt{5}\times\sqrt{5}$ monolayer the sites were equivalent, and so we conclude that the intermediate valence was homogeneous. Furthermore, there seems to be no reason to believe that this condition did not prevail for the hexagonal overlayer too, since the valence varied smoothly with coverage. We attribute the gradual increase in valence to an indirect Sm-Sm interaction mediated by the substrate.

We can in part reconcile the behavior of Sm on Al(001) with that on Cu(001) if we assume that on the former substrate the predominance of the divalent state in a disordered fractional monolayer arose because the Sm atoms were uniformly distributed over the surface. If, on annealing, islands of crystallographic order arose (whence the tendency for streaking at very small coverages) then this, even at small coverages, led to Sm-Sm separations more appropriate to those of complete monolayers with corresponding interactions which favored the 3+ condition. Thus for both substrates the divalent state arose in the isolated adsorbed Sm atom and the intermediate-valent or trivalent states were caused by Sm-Sm interactions. The principle differences between the behavior of Sm on the two substrates then comprise the details of the structural arrangements in the overlayers, the separations of the Sm atoms, and the saturation intermediate valences of 2.95 (Al) and 2.7 (Cu). It is most likely that the filled $3d$ states of the Cu were insignificant for the Sm-substrate interaction; we therefore assume that both Al and Cu substrates may be replaced by a suitable jellium. The energies of the different valence states of Sm are many-particle energies and in the free atom the 3+ state is estimated to lie ~2.4 eV above the 2+.[6] In the presence of the jellium substrate these many-particle states become broadened and experience shifts, in the manner of the Anderson impurity model.[10]. We assume that the progress through the intermediate-valent condition is driven by the broadening and fractional population of the $5d$ orbital. The latter process may be considered in single-particle terms and arises as a combination of a Sm-jellium resonance and indirect Sm-Sm resonances, the latter mediated by the Friedel oscillations in the jellium continuum. The fractional occupation of the $5d$ resonant orbital causes the narrow many-particle resonances to shift and overlap at the Fermi level so that the $4f^5 5d^1 6s^2$ configuration is favored at the expense of the $4f^6 5d^0 6s^2$.

Our data show that for both substrates these changes saturate (but at different values) for Sm separations ~4.5 Å corresponding to coverages ~0.38. The $6s$ states are considered to remain completely filled at all coverages and, initially at least, there is probably very little intra-atomic s-d interaction. Phenomenologically, the fact that on Al(001) we found a saturation valence 2.95 whereas on Cu(001) it stabilized at 2.7 may be associated with the denser electron gas of the aluminum leading to a stronger Sm-substrate interaction as well as stronger Sm-Sm interaction.

Implicit in the above qualitative description is the assumption that there is very little charge transfer between the Sm adsorbate and the substrate. Work-function data for these systems would of course indicate whether this is the case or not.

Independent of this qualitative explanation our results may be taken as a unique and accurate description of homogeneous intermediate valence in Sm. It is clear that the study of such ordered overlayers on substrates of different character may provide much new information and aid in the appreciation of intermediate valence.

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