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Monolayer Sm films on Ta and Cu substrates

L. Tao
Physics Department, New York University, 4 Washington Place, New York, New York 10003

E. Goering and S. Horn
Institut für Physik, University of Augsburg, Memminger Strasse 6, 86159 Augsburg, Germany

M. L. denBoer
Physics Department, Hunter College of The City University of New York, 695 Park Avenue, New York, New York 10021

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We have studied the electronic properties of ultrathin layers of Sm on Ta and Cu substrates using valence-band and resonant photoemission. The average formal chemical valence of Sm on Ta increases from below 2.4 at low coverage to the value measured from bulk Sm at higher coverage, while the valence of Sm on Cu is 3 at low coverage and decreases abruptly to the same value measured for Ta substrates at higher coverage. These changes in electronic properties reflect interlayer and intralayer interactions in these films, particularly the weak Sm-Ta and strong Sm-Cu interactions.

INTRODUCTION

Recent years have seen extensive investigations of rare-earth-based intermetallic compounds, particularly of their magnetic and electronic properties. In this regard those rare-earth-based compounds in which the rare earth exhibits intermediate valence are especially intriguing. In these materials, two distinct electronic configurations of the rare earth are nearly degenerate in energy, and the ground state of the system must be described as a quantum-mechanical mixture of the two. This near degeneracy is observed in many compounds involving a rare earth, such as europium, samarium, and ytterbium, with an electron shell which is close to either completely filled, completely empty, or half-filled. Due to this degeneracy, the electronic configuration (or formal chemical valence) of the rare earth in these compounds depends sensitively on the chemical environment, as well as on external parameters such as temperature and pressure, and the physical structure, including the presence of a surface. The electronic configuration of the most weakly bound electrons includes both localized $4f$ electrons which are chemically inactive and extended $5d$ and $6s$ electrons which participate in bonding. We use the term "valence" here to denote the occupancy of the latter orbitals.

For example, in Sm metal the Sm^{2+} or $4f^6\,(5d6s)^2$ configuration is nearly energy degenerate with the Sm^{3+} or $4f^5\,(5d6s)^3$ configuration, due to competition between the stability of the half-filled f shell and the cohesive energy term in the solid state. Thus in many Sm-transition-metal intermetallic compounds Sm is in an intermediate valent state, a superposition of the Sm^{2+} and Sm^{3+} configurations. Although bulk metallic Sm is trivalent, at the surface the cohesive energy which favors the Sm^{3+} configuration is weaker due to the reduced coordination. Therefore, those Sm atoms at the surface are divalent or mixed valent, as has been demonstrated by photoemission.[1] As the radius of divalent Sm is about 15% larger than that of trivalent Sm,[2] this should have significant structural ramifications. However, direct evidence has been lacking, probably due to the difficulty of preparing single-crystal Sm surfaces, although recently low-energy electron-diffraction (LEED) measurements on epitaxial Sm layers on Mo(110) have provided evidence for this transition.[3]

Sm, like other rare earths, has a low surface tension[4] and one expects layer-by-layer growth on many substrates. Given the sensitivity mentioned above, the valence of Sm in such films should depend on the structural properties of the layers. Such effects are indeed observed. Thin layers of Sm on C are formally divalent, but thicker Sm layers become trivalent.[5] On Nb, Sm is also trivalent, although an initial divalent state is observed shortly after deposition.[6] Monolayer growth was observed by Fäldt and Myers for Sm on a variety of substrates. At submonolayer coverage, Sm on Al(100) (Refs. 7 and 8) and Al(110) (Ref. 9) was found to have an average valence of 2.4–2.6, while an ordered monolayer was predicted to be trivalent. On Cu(100), these authors found that ordered monolayers of Sm were formed.[10] Both the structure of these layers and the electronic state of the Sm ions were reported to be sensitive to the Sm coverage, illustrating the importance of both interlayer (Sm-Cu) and intralayer (Sm-Sm) interactions in determining the ground state of the system. The Sm appeared to be in a mixed-valent state, which could be either heterogeneous or homogeneous. As ordered overlayers were formed, these authors concluded that the system was homogeneous; that is, all Sm ions were in the same mixed-valent state. However, Anderson *et al.*[11] studied the $4f$ levels of Sm on Cu(100), and found that the $4f$ multiplet closest to the Fermi level E_F had a binding energy greater than 0.5 eV. If the Sm was a homogeneously mixed valent, this multiplet would be energy degenerate with the $4f^{n-1}$ state and at most 0.4 eV below E_F. Moreover, it was pointed out that the Sm-Cu phase diagram suggests that compounds should form with trivalent Sm.[11] These authors therefore suggested[11] that the Sm/Cu system in fact consists of bulk layer(s) containing trivalent Sm formed by reaction with the Cu substrate plus a divalent Sm surface layer. This conclusion is supported by the observation by Wieliczka and Olson[12] that Cu may diffuse through relatively thick layers of Sm in times of the order of a few hours at room temperature. On the other hand Jørgensen, Christiansen, and Onsgaard[13] reported the formation of ordered Sm overlayers, including reconstructions, on all three low-index planes of Cu.

Compound formation is unlikely for Ta substrates; while several Sm-Cu compounds exist (in which Sm is formally trivalent), the Sm-Ta phase diagram lists no compounds, and Sm is negligibly soluble in Ta even above room temperature, indicating the absence of strong attractive Sm-Ta interactions. Moreover, Ta has a much higher surface tension than Sm. Therefore, interdiffusion is likely to be small and layer-by-layer (Frank–van der Merve) growth should occur.

Here we describe photoemission measurements of submonolayer to several-monolayer Sm films formed on polycrystalline Ta and Cu substrates, as well as on Cu(110). Using energy-dependent photoemission, we were able to observe both the chemical state of the Sm and the behavior of the Ta or Cu substrate as a function of coverage. On Ta, at low Sm coverage, the system appears to consist essentially of isolated Sm ions interacting weakly with the substrate. As the coverage increases, the effects of Sm-Sm intralayer interactions become more important. On the other hand, on Cu, the effects of substrate interactions appear to dominate at all Sm coverages. Given the strong Sm-Cu interaction, compound formation is possible.

EXPERIMENT

The experiments were carried out in a UHV chamber with a base pressure of about 10^{-10} torr. Photons were obtained from the vacuum ultraviolet (vuv) ring of the National Synchrotron Light Source at Brookhaven National Laboratory. We used the Howells-type plane-grating monochromators at beam lines U7B and U14, which have a typical resolving power $E/\Delta E$ of 100. The photoelectrons were measured by an angle-resolving 50-mm sector analyzer typically operated with a fixed pass energy of 20 eV for an energy resolution of about 0.2 eV, or by a commercial cylindrical mirror analyzer with similar resolution. Spectra are plotted relative to E_F. The single-crystal Cu substrate was cleaned by sputtering with 1000-eV Ar ions. To obtain a LEED pattern, it was thereafter annealed, typically for several hours at ~700 °C. To study the effect of surface roughness, on several occasions, as noted below, the sample was not subsequently annealed. Many sputtering and evaporation cycles were required to obtain a clean Cu surface. The Ta was cleaned by repeated cycles of high-temperature treatment and oxygen annealing. As this high-temperature flashing eventually recrystallizes the Ta, the substrate probably consisted largely of (110) facets.[14] Sm of 99.99% purity was evaporated onto the Cu substrate. Sample cleanliness was monitored by Auger-electron spectroscopy and by low-energy photoemission. We particularly checked for the presence of oxygen, especially on Sm-covered surfaces, by measuring representative films after brief exposure to oxygen, or overnight exposure to the ambient pressure in the vacuum chamber for comparison. Spectra measured from such surfaces differed from those measured from clean surfaces, indicating that our surfaces are free of oxygen. During the deposition of Sm (evaporated from resistively heated tungsten baskets) the pressure rose to typically 2×10^{-9} torr, and it fell quickly when evaporation was completed, assisted by the gettering action of Sm on the chamber walls. After measurements were completed on a layer of given thickness, the sample was cleaned before a new film was deposited.

Measurements were made as a function of Sm film thickness. Different coverages were obtained by varying the evaporation conditions, i.e., source temperature and evaporation time. The Sm coverage was obtained by observing the attenuation of substrate peaks in the photoemission spectra due to the pressure of an overlayer. The measured intensity N_L of a substrate peak measured when the substrate is covered by a Sm layer of approximate effective thickness L is related to the intensity of the substrate peak measured on the clean substrate, N_0, by

$$N_L = N_0 e^{-L/\lambda} , \tag{1}$$

where λ is the photoelectron mean free path in the Sm. Using tabulated values for λ, L can be obtained from measurements of N_0 and N_1. As the incident photon flux, geometry, etc., vary uncontrollably between spectra, we first normalized each peak to a smooth region in the spectrum far from any photoemission peak. For ultrathin films, this procedure should give good relative coverage estimates, as long as the growth is layer by layer. However, systematic errors will be present, for example due to the necessity to estimate λ, and higher coverages will be overestimated due to the normalization technique.[15] The procedure is illustrated in the corresponding experimental sections.

RESULTS: Sm/Ta

Figure 1 shows spectra of the Ta substrate, both clean and after exposure to 0.1 L of oxygen, measured at incident photon energies of 80 and 40 eV chosen to improve the resolution. Evidently, there are at least three distinct contributions to the Ta spectrum. All are due to emission from Ta 5d states, as has been shown by resonant photoemission.[16] The intensity closest to the Fermi energy E_F is attributed to bulk states. The two additional contributions, one at a binding energy $E_B = 1$ eV and another at $E_B = 3$ eV, are ascribed to Ta surface states. In the spectrum taken with an incident energy of 80 eV only the surface state at $E_B = 3$ eV can be resolved. Exposure to 0.1 L of oxygen (not shown here) has virtually

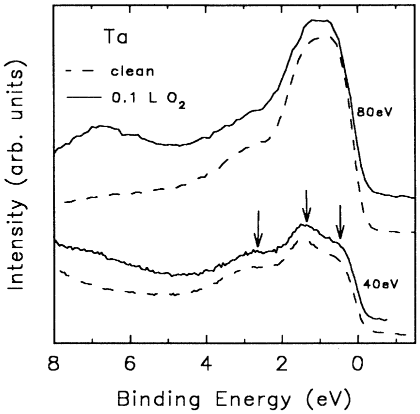

FIG. 1. Energy distribution curve (EDC) of (a) clean Ta; (b) Ta exposed to 0.1-L O_2, measured at a phonon energy of 50 eV; and (c) clean Ta at 40 eV.

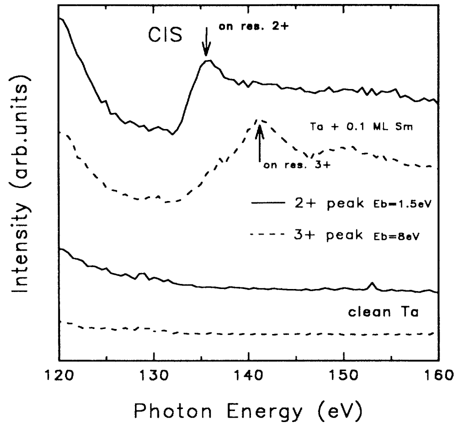

FIG. 3. Constant-initial-state (CIS) spectra of Ta plus 0.1 monolayer of Sm, illustrating the "giant" $4d->4f$ resonance.

no effect on this state, or on the Ta $4d$ spectrum, although the presence of O is confirmed by the prominent peak which forms at 7 eV due to emission from O $2p$ states.[17]

In Fig. 2 we illustrate the main features of Sm overlayers on Ta. This figure compares the spectra of clean Ta at incident photon energies of 60 and 180 eV, with a Ta surface covered by about 1.3 monolayers of Sm taken at 180 eV. These spectra demonstrate the strong decrease of the Ta $5d$ intensity at higher energies, where the more localized Ta $4f$ contributions at $E_B=21$ and 24 eV dominate, as predicted by cross-section calculations.[18] The additional intensity in the spectrum of Sm-covered Ta near the Fermi level (shown on an expanded scale in Fig. 6) is due to Sm $4f$ contributions which mask the Ta $5d$ emission near E_F. The Sm $4f$ peak at $E_B=1.5$ eV corresponds to the Sm $4f^6 \Longrightarrow 4f^5$ transition (Sm^{2+} initial state), and that at $E_B=6$ eV to the Sm $4f^5 \Longrightarrow 4f^4$ transition (Sm^{3+} initial state).[3]

This assignment may be confirmed by constant-initial-state (CIS) measurements, in which the binding energy is held fixed as the incident energy is varied. In Fig. 3 we plot the intensity at $E_B=1.5$ (Sm^{2+}) and 6 eV (Sm^{3+}) measured on Ta, both clean and covered by 0.1 monolayers of Sm. For clean Ta, a monotonic decrease is observed, reflecting simply the decreasing Ta $4d$ cross section in this energy range.[18] On the other hand, as also shown in Fig. 3, on the Sm-covered surface the emission from trivalent and divalent Sm show prominent maxima near the Sm $3d$ binding energy, at incident energies of 136 and 141 eV, characteristic of the Coster-Kronig resonances of divalent and trivalent Sm, respectively.[19] We refer to the maximum in each case as "on" resonance, while the preceding minimum is "off" resonance. These "giant" resonances are well known in the rare earths, and the energies are characteristic of the ground-state electronic configuration. The presence of *both* peaks at this Sm coverage indicates that the Sm is either in an homogeneous intermediate valence state, or that Sm ions occupy inequivalent sites with different cohesive energies, resulting in different valence states of the Sm ions, or both.

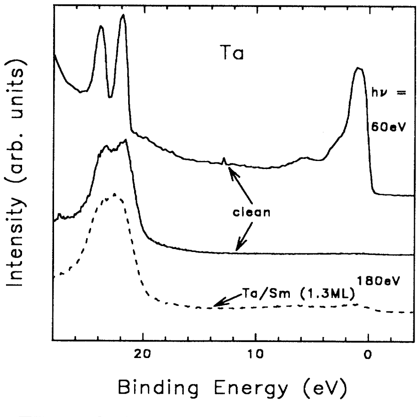

FIG. 2. EDC of clean Ta measured at (a) $\hbar\omega=60$ eV; (b) $\hbar\omega=180$ eV; and (c) Ta plus 1.3 monolayer Sm at 180 eV.

To understand the relative importance of interlayer and intralayer interactions in determining the Sm configuration, it is instructive to make these measurements as a function of Sm coverage. This requires measuring the Sm coverage and quantifying the "average" Sm valence at each coverage. Determining the absolute coverage of an overlayer is difficult, particularly in this case where the deposition rate is not constant and direct methods such as a crystal rate monitor are unsuitable. As described above, the attenuation of photoemission peaks can be used to determine the relative coverage. The procedure used for the Ta substrate is illustrated in Fig. 4(a). For each Sm film, we measured the Ta $4f$ photopeak at a photon energy of 180 eV, where it is quite intense and well separated from other features in the spectrum. We then assume that the Ta $4f$ peak intensity, at a given Sm coverage, is given by Eq. (1). In this case, N_1 is the Ta $4f$ intensity at a given Sm coverage of thickness L, N_0 the Ta $4f$ intensity on clean Ta, and λ the escape depth of the Ta $4f$ electrons through the Sm layer. These electrons have a kinetic energy of ~ 150 eV at this photon energy, and from tabulations we estimate $\lambda \approx 5$ Å.[20]

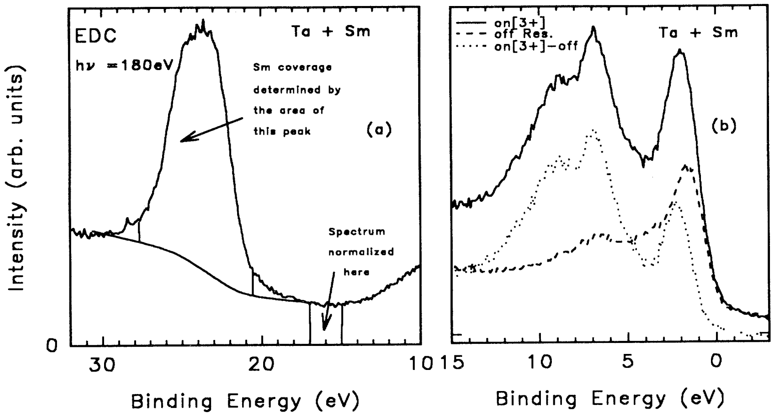

FIG. 4. EDC of Ta, illustrating how the Sm coverage was determined.

The intensity N of the $4f$ peak was estimated by first subtracting a background proportional to the emission at higher energy (Shirley background) and then computing the area of the remaining peak. This was normalized to the photoemission intensity in the binding energy range 15–17 eV, which is structureless and presumably proportional to the incident beam. The coverage L can be converted to an equivalent number of monolayers of Sm atoms at the mean bulk interatomic spacing of 3.59 Å.

We obtained a measure of the relative amount of divalent and trivalent Sm in two ways. One method exploits the different photon energy dependence of divalent and trivalent Sm. We measured the photoemission spectra of each film at the "on" resonance energy (see Fig. 3) of Sm^{2+} and Sm^{3+}, respectively. A representative result is shown in Fig. 4(b). We also measured the "off" resonance spectrum at 126 eV, where the Sm $4f$ emission has a local minimum. This "off" spectrum for each film was subtracted from the two "on" spectra, as also shown in Fig. 4(b). The results for a series of films of different thickness are shown in Fig. 5. It is evident that at low coverage the Sm is predominantly divalent. As the coverage increases, the proportion of trivalent Sm increases, until for very thick films trivalent Sm dominates, presumably approximating the situation for pure Sm. For quantitative estimates, the Sm^{2+} (Sm^{3+}) intensity was taken to be the integrated intensity of the 0–2 eV (5.5–7.5-eV) binding-energy region after background removal.

In another method of obtaining the "valence," we measured the spectra at an incident photon energy of 180 eV, normalized to the valley between the Ta $4f$ and Sm $4f$ emissions. This procedure neglects changes in the Ta emission due to the presence of Sm; as discussed below, such changes, while observed, were too small to significantly affect coverages estimates. Representative spectra are shown in Fig. 6. The same trend of an initially divalent layer becoming more trivalent is observed. As before, we integrated the emission from 0–2 eV (5.5–7.5 eV) as a quantitative measure of the divalent (trivalent) signal.

To quantify the qualitative changes in Sm electronic structure illustrated by these measurements, we computed the "average valence" defined as

$$V_{\mathrm{avg}}=\frac{3I_3}{I_3+I_2}+\frac{2I_2}{I_3+I_2}\ , \tag{2}$$

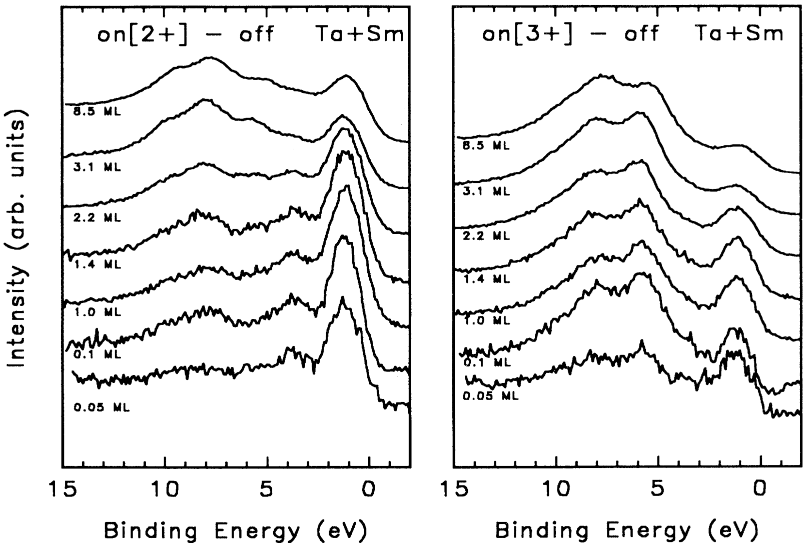

FIG. 5. "On-resonance" and "on-resonance–off-resonance" spectra of Sm layers of varying thickness as indicated, deposited on polycrystalline Ta.

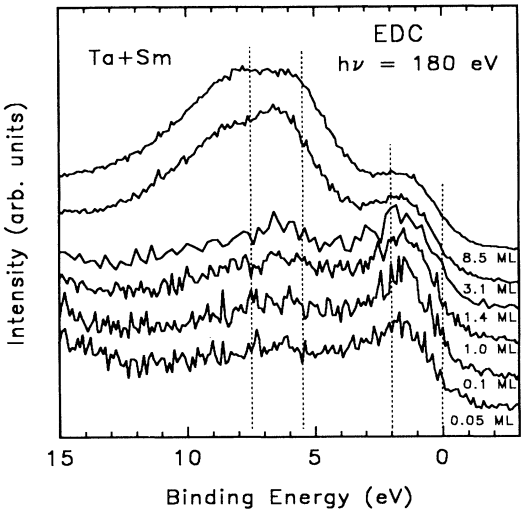

FIG. 6. EDC's of Sm layers of varying thickness as indicated, measured at $\hbar\omega = 180$ eV.

where I_3 and I_2 are the intensities of the 3^+ and 2^+ states, respectively, measured using the methods just described. The results are shown in Fig. 7. Evidently, V_{avg} changes with coverage, with a minimum value of 2.37 at the lowest coverage, and increases slowly to 2.70, the average valence measured on pure Sm using similar electron energies. The random and systematic errors in these valence values are probably about 20%, but the trends are clear from Fig. 7.

RESULTS: Sm/Cu

The photoemission spectrum of clean Cu measured at a photon energy of 150 eV is illustrated in Fig. 8. The possible presence of O would be indicated by a peak at 7 eV, corresponding to emission from the O $2p$ level, which is particularly prominent at low energy, as illustrated in Fig. 1. No such peak is found on our clean Cu samples. The prominent peak in the spectra of Fig. 8 is due to emission from the Cu $3d$ band; this makes it more difficult to distinguish features due to Sm $4f$ emission, which fall in the same energy region. In contrast to Ta, emission from the Cu $3d$ band is prominent at all available photon energies. Figure 8 also illustrates the determination of Sm coverage using attenuation as described in Eq. (1). In this case, the Cu $3p$ intensity was measured at a photon energy of 150 eV. This was taken to be the area under the peak as shown, divided by the intensity in the binding energy range 20–25 eV. At the corresponding photoelectron kinetic energy ~ 75 eV, the electron mean free path $\lambda \approx 5$ Å, and for the Ta substrate we use the mean bulk Sm interatomic spacing to convert to equivalent monolayers.

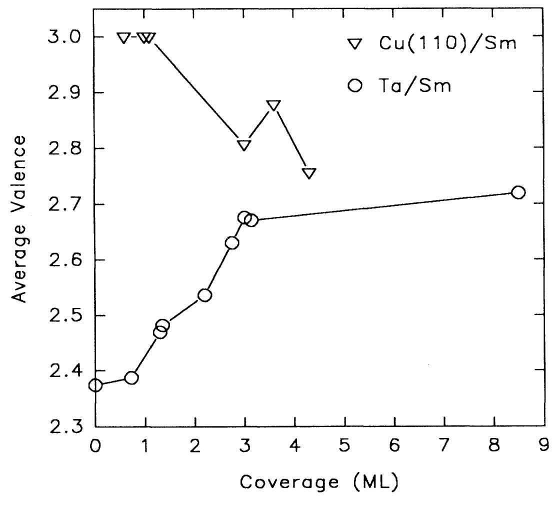

FIG. 7. The valence of Sm on Ta and Cu, measured as described in the text, as a function of Sm thickness.

One can exploit the different photon energy dependence of the Cu $3d$ and Sm $4f$ emissions to separate their contributions to the photoemission spectra, as was done for the Ta substrate. This is illustrated in Fig. 9, where we plot the emission from the clean Cu(110) crystal and that from Sm-covered Cu as a function of photon energy. The Cu shows only a monotonic decrease characteristic of the Cu $3d$ photoemission cross section in this energy region, while the Sm emission shows peaks at the trivalent and divalent resonant energies as for the case of Sm on Ta described in Fig. 3. The shape of the resonance here differs from that in Fig. 3, due both to intrinsic factors such as the Sm valence state, and extrinsic ones such as background variations.

In Fig. 10 we show representative photoemission spectra measured at the Sm^{3+} resonance energy of 141 eV. At low coverage, the spectra are dominated by the Cu $3d$ peak. Nevertheless, the absence of a Sm^{2+} signal at low coverage indicates that on Cu(110) Sm is trivalent for coverages less than one monolayer (ML). At higher coverages a Sm^{2+} signal appears abruptly, indicating a decrease in the average valence. The Cd d feature is wider in the spectrum of Sm-covered Cu than in that of clean Cu, presumably due to broadening of the Cu d band by interaction with Sm.

These effects are also observed in the CIS measurements shown in Fig. 11, also taken from Sm deposited on Cu(110). Here we plot CIS spectra taken at the binding energy of the most prominent 3^+ and 2^+ features, respectively. At low coverages a resonance is observed at the Sm^{3+} resonant binding energy, but not at that of Sm^{2+}, confirming that the surface layer contains primarily trivalent Sm. This is especially apparent for a coverage of 1.1 ML. Only at coverages larger than one monolayer does a resonance due to divalent Sm appear. To confirm that these results are not due to crystalline orientation effects, we have also performed these measurements for Sm deposited on "roughened" Cu, prepared by sputtering the Cu to obtain a clean surface, but without subsequent annealing. Similar effects were observed: At low coverage, the Sm was close to trivalent, and at larger coverage the average valence decreased.

The results of these measurements on Cu are summarized in Fig. 7. We plot here the "valence" of Sm,

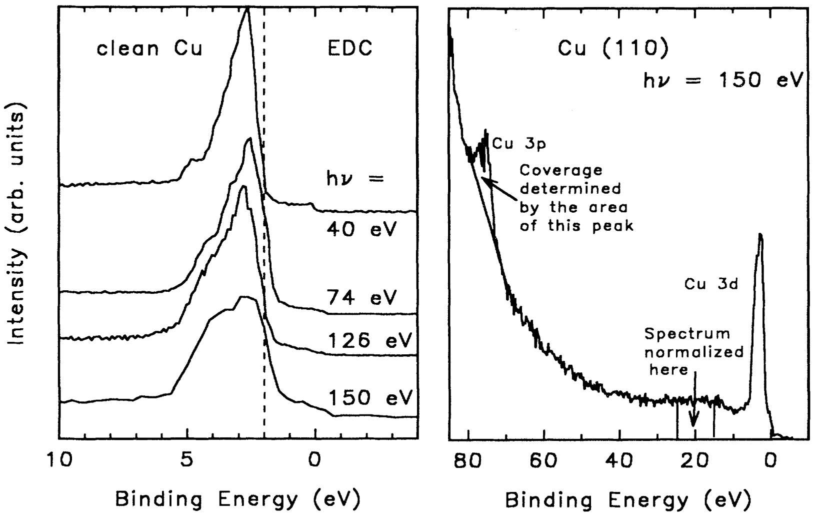

FIG. 8. EDC of clean Cu taken at 150 eV, illustrating how the Sm coverage was obtained, and corresponding spectra at the indicated photon energies, showing the dominant Cu 3*d* emission.

defined as for the Ta substrates by Eq. (2), as a function of Sm coverage. There is evidently good agreement between measurements on the single-crystal Cu surface and those on the disordered surface, indicating that the changes observed do not depend on the structure of the surface. The Sm valence remains about 3^+, indicating a $4f^5$ electronic configuration, below a coverage of one monolayer; at higher coverages, the valence changes rather abruptly to nearly the value observed for bulk samples of Sm.

DISCUSSION

We discuss first the results for Sm films on Ta, then those on Cu, and finally we compare the two. Figure 7 shows that the average valence of Sm at low coverage on Ta is about 2.37. This value is lower than the average valence of Sm atoms at the surface of Sm, and much smaller than the value on Cu (Ref. 11) or Al,[21] and it indicates that the Ta-Sm interaction is weak. As the Sm coverage increases, the Sm valence increases as well. This shows that on the Ta surface the Sm-Sm interaction is attractive enough to shift the competition between atomic energy terms (which favor divalency) and cohesive energy terms (which favor trivalency) toward the latter, as described in Sec. I. In the limit of a very thick film, we presumably recover the situation of a trivalent bulk and a divalent or mixed-valent surface.

The surface layer of Sm may be either homogeneously

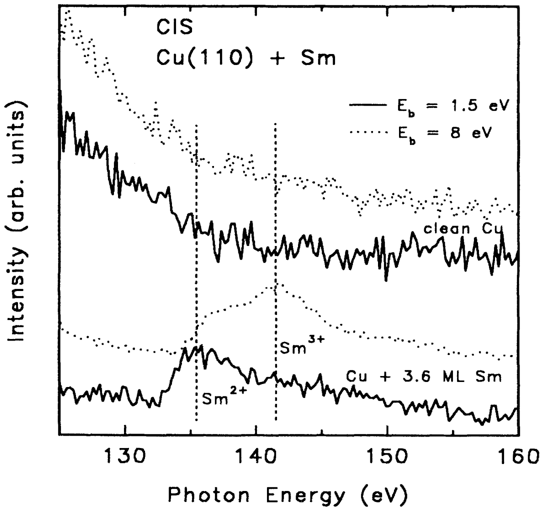

FIG. 9. Constant-initial-state spectra of clean and Sm-covered Cu, illustrating the monotonic decrease in Cu *d* emission and the Sm resonance.

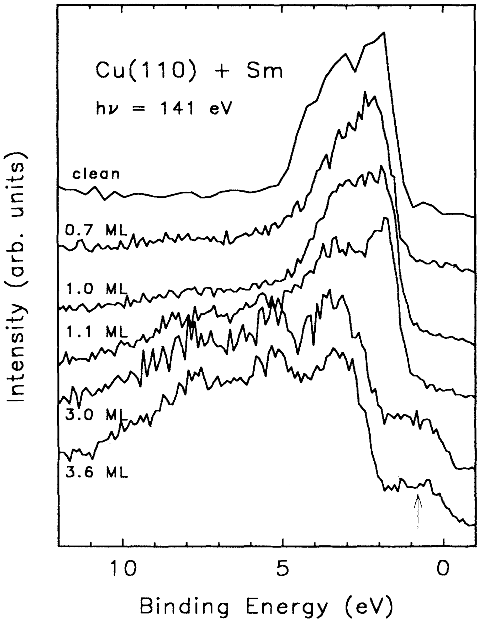

FIG. 10. EDC's of Cu(110) plus Sm at the coverages indicated, taken at the resonant photon energy of the 3+ multiplet. The arrow indicates the location of the 2+ multiplet present at higher coverage.

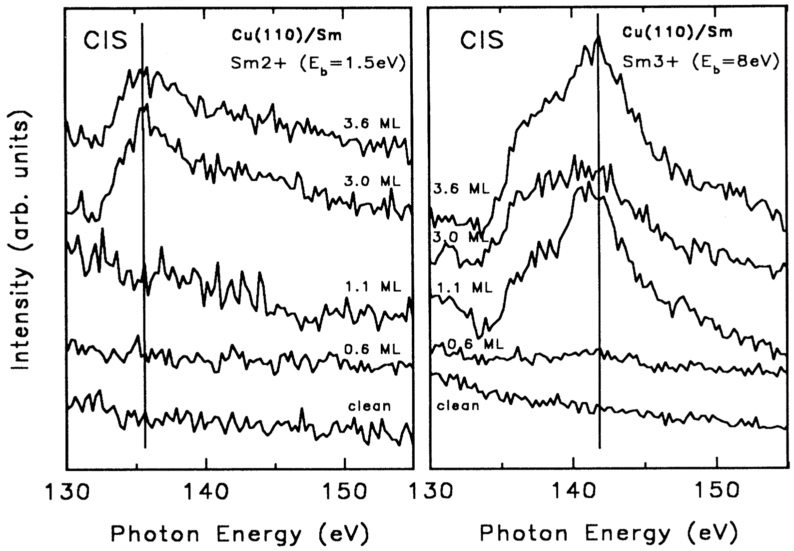

FIG. 11. CIS spectra of the most prominent Sm^{3+} and Sm^{2+} multiplets of CU(110)/Sm at the coverages indicated.

mixed valent or it may be heterogeneous, with Sm ions in various different configurations. As discussed above, these measurements cannot distinguish between these possibilities. If the Sm is homogeneously mixed valent, the average valence evidently changes with the coverage. There are, of course, a number of examples of valence differences between the surface and the bulk in intermetallic compounds, including $SmAl_2$ (Ref. 22) and SmB_6.[23] The common feature of these materials is that the competition between the cohesive and atomic terms leads to a near-energy degeneracy and a quantum-mechanical mixture of the two configurations in the ground state. Rather small changes in the cohesive energy can therefore lead to a shift in the relative energy of each configuration and a consequent shift in the average occupancy and the observed average valence.

The other possibility is that the Sm is inhomogeneously mixed valent. This might be due to the presence of more than one kind of site on the Ta surface, which may give rise to Sm in different electronic states because of differing substrate interactions. The Ta surface used was polycrystalline, so the possibility exists that, particularly at low coverage, Sm will preferentially occupy sites such as defect sites near grain boundaries. However, at coverages on the order of a monolayer, the number of such sites available is probably too small to account for the observed Sm valence. Virtually all Sm surface sites would have to be such defect sites, which seems unreasonable. It is also possible that the Sm occupies more than one site on the crystallographic Ta surface, which as mentioned above probably consisted of (110) planes. While no structural studies (LEED, etc.) have been carried out on this surface, it seems improbable that Sm would occupy more than one site on the dense, symmetric, (110) surface of bcc Ta, but the possibility cannot be ruled out.

Another model which leads to inhomogeneous mixed valence is the following. Assuming, for reasons given above, Frank–Van der Merve growth of Sm on Ta, it could be that at coverages below one monolayer, Sm islands of varying size form on the Ta surface. Due to the sensitivity of the Sm valence to the cohesive energy, the Sm atoms at the edges of these islands could have a different valence than those in the interior of the islands. With increasing coverage the ratio of edge to interior atoms decreases until a complete monolayer is formed. A further shift to trivalency will probably occur for Sm atoms in the first monolayer when the second Sm layer starts to develop, again due to the increase in the cohesive energy term for atoms in this layer. Another effect pushing the second layer closer to trivalency then the first is the stronger Sm-Sm interaction compared to the Sm-Ta interaction. Since our photoemission experiments measure a surface layer about three monolayers thick, the Sm valence should therefore saturate for coverages above three monolayers at the value observed for Sm bulk material. This is consistent with our observations, which in this model are then due to Sm in different sites (edge and interior) whose relative numbers change.

The behavior of Sm on Cu is also shown in Fig. 7. Note that the Sm-Cu phase diagram shows a large number of Sm-Cu compounds, reflecting a strong Sm-Cu interaction. The results of Fig. 7 show that, at low coverages, the Sm is essentially trivalent. This is in contrast to the observations of Fäldt and Myers,[10] who found that thin layers of Sm on Cu(001) were divalent, changing to mixed valence as the thickness increased. The (110) surface of fcc Cu is slightly more open than the (001), so that, at low coverage, a typical Sm ion can be in close contact with several surface Cu atoms. Given the attractive Cu-Sm interaction, this increased coordination is likely to drive the Sm in the direction of increased charge transfer, hence trivalency, and something approaching a surface Sm-Cu compound may form. As the Sm coverage increases, the average Cu-Sm coordination in the surface region must decrease, and we observe that the average valence correspondingly drops. It may be that the relatively stable surface compound limits diffusion of Sm into the bulk, increasing the amount of Sm in the surface region and eventually building a surface layer similar to the surface of pure Sm.

The behavior of Sm on Cu is quite different from its behavior on Ta. The differences are evidently due to the different strengths of the Ta-Sm and Cu-Sm interactions. The former is weak, so that thin layers of Sm on Ta are nearly divalent. It happens that the electronic state of Sm is dominated by Sm-Sm interactions. The Cu-Sm interaction is strong, so that significant charge transfer to the Cu occurs and the Sm valence increases to 3. On the other hand, the fact that, on Cu, the Sm valence does not change with Sm coverage (for small coverages) indicates that interlayer Sm-Sm interactions are not important, in contrast to the case of Ta as a substrate, where they are strong enough to gradually increase the Sm valence to the value measured on pure Sm. On Cu, the only effect of increasing thickness is to eventually form a true "surface" layer of Sm, which is presumably separated by at least one monolayer from the Cu substrate, thus facilitating the formation of the mixed-valent layer eventually observed.

SUMMARY

These measurements show that the interlayer and intralayer interactions of Sm on Ta and Cu substrates are very different. On Ta, the electronic state of Sm is dominated by Sm-Sm intralayer interactions, but on Cu substrate-overlayer interactions dominate at low coverage, driving the Sm to trivalency. Photoemission proves to be a sensitive monitor of these changes in surface electronic properties. Additional measurements, particularly investigations of the physical structure of Sm on Ta and Cu single-crystal surfaces, and the effect of Sm overlayers on Ta surface states, are necessary to give a complete picture of these interactions.

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