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3*d* photoemission study of the intermediate valence of Sm on Si(001)

Å. Fäldt and H. P. Myers
Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

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Overlayers of Sm on Si(001) were studied by x-ray photoemission spectroscopy and low-energy electron diffraction. Divalent Sm was observed in the low-coverage region, while an average valence of ~2.75 was observed for monolayer coverage. It is concluded that except for very low coverages the variation of the Sm valence is controlled by direct Sm-Sm interaction. A comparison between the Sm-coverage dependence of 3*d* spectra and previously obtained 4*f* spectra gives further evidence to the view that photoemission from Sm core levels gives reliable information about the valence.

Photoemission spectroscopy has frequently been used to study the valence of Sm metal and the purported intermediate valence of this element rests on the occurrence of replicate spectra arising from two different initial states for the Sm atom.[1-8] This intermediate valence of Sm metal is usually attributed to a wholly or partially divalent surface layer. However, as demonstrated in the calculations by Herbst and Wilkins[9] and Herbst, Burkstrand, and Wilkins,[10] satellite spectral structure originating from different final states derived from the same 3+ initial state is indistinguishable, energywise, from replicate spectra derived from different (3+, 2+) initial states.

Even so, in studies of the lighter rare-earth metals La, Ce, Pr, and Nd, what are considered to be true satellite peaks are always found to have an intensity less than 5% of that of the main peak. Furthermore, the intensity of the satellite peak decreases with increasing atomic number and is expected to be very small in Sm metal.[8] Similar conclusions are drawn from a systematic study of the intermetallic compounds $R\text{Pd}_3$ (R = La, Ce, Pr, Nd, and Sm); the satellite being undetectable in SmPd_3.[11] On the other hand, an L_{III} absorption study of EuPd_2P_2 (Ref. 12) is interpreted in terms of final-state effects in the light of other nonspectroscopic evidence. It must be admitted, however, that the latter compound is far removed from the pure rare-earth metal. In the particular case of Sm metal for which, as a conventional evaporated film, the extra (replica) line has an intensity ~25% of that of the main line there seems little reason, as yet, to conclude other than its indicating the presence of the divalent state in the surface layer(s).

On the assumption that the 3*d* photoemission spectrum of Sm is a replicate spectrum arising from the occurrence of both 3+ and 2+ valence configurations in the initial state, we have earlier studied the valence of Sm in ordered overlayers formed on Al(001) and Cu(001) substrates.[13-15] Whereas disordered overlayers of Sm on Al(001), particularly at submonolayer coverages, show distinct intermediate valence ~2.5, three different structurally ordered overlayers all have the valence 2.95. Similar studies with Sm on Cu(001) show that the valence varies smoothly with coverage starting at a value of two at extreme dilution and rising to a saturation value of 2.7 at monolayer and higher coverages. The different behavior of Sm on these two surfaces may in part be associated with the different forms of monolayer growth in the two systems. In the complete monolayers, for both substrates, the Sm-Sm separations range from 3.6 to 4.5 Å; these separations are compatible with direct Sm-Sm interactions as a cause of the variation in valence. At very low coverages, however, and particularly in disordered overlayers, it seems necessary to assume that Sm-Sm interaction is mediated by the substrate. It is therefore of interest to study Sm overlayers formed on substrates with widely different electronic structure. It is also the case that overlayers of the kind found on Al(001) and Cu(001) have the advantage of there being only one layer of rare-earth metal; thus there is no uncertainty, as with bulk Sm metal, as to whether the intermediate valence extends beyond the first layer. Another advantage is that the valence of Sm in such layers can show a wide range of variation. In contrast to the metals Al and Cu, we therefore chose to study Sm overlayers on Si(001).

Franciosi *et al.*[16] have earlier investigated the 4*f* photoemission spectrum of Sm deposited onto a Si(111) substrate. No crystallographic observations were made, but they conclude that a Sm film ~2–3 Å thick is divalent and the valence increases for thicker films. No absolute measure of coverage or thickness was made.

Our experimental technique was similar to that described earlier[15] being based on a Vacuum Generators x-ray photoemission spectrometer (XPS) fitted with a three-grid low-energy electron diffraction (LEED) unit and an ion gun for cleaning purposes. The Si(001) substrate was cut from an *n*-doped (10–50 Ω cm) 0.4-mm-thick wafer. It could be cooled to ~ −160 °C and directly heated by the passage of electrical current through it. The temperature was measured by a thermocouple and an optical pyrometer. Prior to all measurements the Si(001) substrate was cleaned by argon-ion bombardment (5 kV, 50 μA) and then heated to ~850 °C to remove lattice disorder. It was thereafter cooled to below room temperature within two minutes. This procedure gave a sharp two-domain $c(4\times2)$ LEED patttern with intense quarter-order spots. Sm was evaporated from a tungsten boat heated by electron bombardment. The base pressure in the experimental chamber was 1.0×10^{-10} mbar and evaporation of Sm caused a momentary increase to 1.0×10^{-9} mbar. Any influence of residual gases on the Sm layers was insignificant, and the data to be presented are considered characteristic of clean Sm overlayers. XPS data were obtained with unmonochromatized Al Kα radiation (correction for the presence of $\alpha_3\alpha_4$ satellites is made). Counting times were ~10 min. Attention was directed to the $3d_{5/2}$ spectrum; the component with binding energy near 1081 eV being associated with the 3+ initial state and that near 1074 eV with the 2+ state.

In Fig. 1 we depict the $3d_{5/2}$ spectrum for four different Sm films. The data were obtained under identical conditions and in all cases the substrate was held at ~ −160 °C during deposition of the Sm and its subsequent study. No ordered overlayers of Sm were observed when the Si(001) substrate was held at or below room temperature. At the lowest coverage the Sm is predominantly divalent, but increasing coverage leads to a progressively higher valence which eventually saturates at a value ~2.75. Since the Sm overlayers were disordered, we cannot determine a coverage directly. However, lack of crystalline order implies the absence of diffusion, and for submonolayer coverages all the Sm atoms deposited lay on the substrate surface, so they all contributed to the photoemission signal. We may therefore plot the valence of the Sm as a function of the total $3d_{5/2}$ photoemission signal, which in turn is a measure of the total amount of Sm deposited. Furthermore, using earlier data for Sm on Cu(001) obtained under similar counting conditions and for which the coverages and Sm concentrations are known, we may, through a comparison of the total signal intensities obtained for the two substrates, estimate the concentration of Sm atoms on the Si(001) substrate. The variation of observed valence with coverage of the Si(001) so determined is shown in Fig. 2. The implication is that the isolated Sm atom on the Si(001) is divalent. The valence increases smoothly with coverage attaining the saturation value 2.75. The pattern of behavior is similar to that for Sm on Cu(001) with the difference that the present overlayers remain disordered. No shift in energy of the Si $2p$ line was observed indicating only weak interaction between Sm and Si.

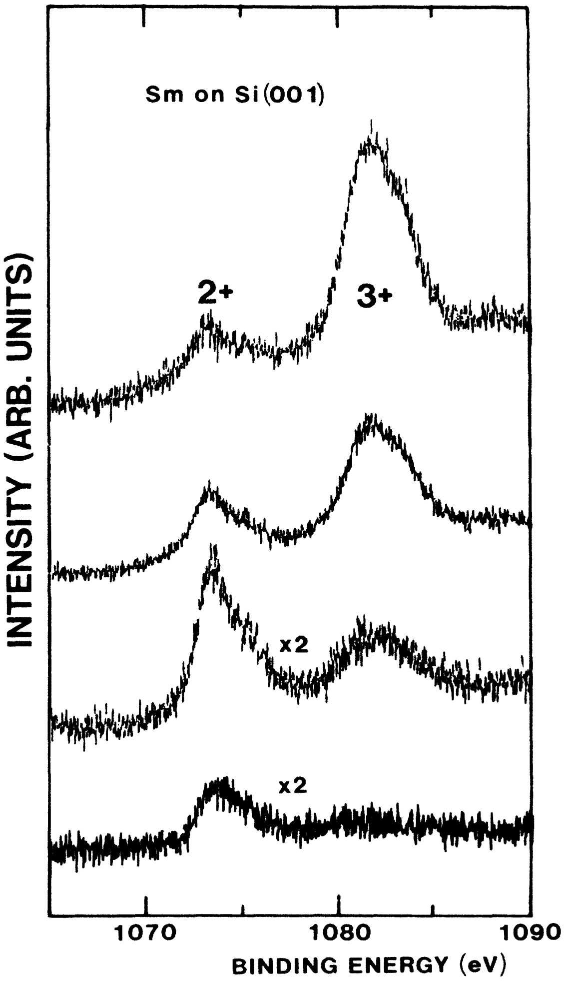

FIG. 1. The x-ray photoemission spectrum of the $3d_{5/2}$ lines for different coverages of Sm on Si(001) taken with Alkα radiation. The coverages are (from the botton) 0.05, 0.2, 0.5, and 1.0, respectively. (A coverage of unity corresponds to one Sm atom per Si atom.)

After heating the substrate to ~600 °C a Sm(2×1) was observed in LEED [the notation being based on a nonreconstructed Si(001) surface], but the situation was complicated by the diffusion of Sm into the Si. Thus Fig. 3 shows the *Sm*$3d_{5/2}$ spectrum of a disordered overlayer before annealing and for the same layer after different times at 600 °C. [No attempt was made to determine the minimum temperature at which a (2×1) Sm structure could be formed.] It is seen that the total spectral intensity decreases with increasing holding time at the high temperature due to intermixing of the two elements. (For the metallic substrates Al and Cu, annealing of Sm overlayers at equally high temperatures did not lead to a decrease of the concentration in the surface region.) On this account we are unable to estimate the valence of the Sm in the ordered structure, because Sm atoms below the outermost surface layer contributed to the signal strength (we estimate the photoelectron mean free path to be ~8 Å). It is clear, however, that the total intensity decreases; atoms of Sm are removed from the surface leading to a lower coverage and an overall decrease in the valence. Thus the variation of valence with coverage is reversible.

We reiterate our belief that the behavior of the $3d$ spectrum is reflecting initial-state effects. Such belief is supported by the comparison of $3d$, $4d$, and valence-band spectra of Sm metal reported by Wertheim and Crecelius[2] and more particularly by the observation of the divalent $4f$ spectrum for small amounts of Sm deposited on Si(111).[16] The variation of valence with coverage for disordered submonolayer films of Sm on Si(001) is very similar to that observed for

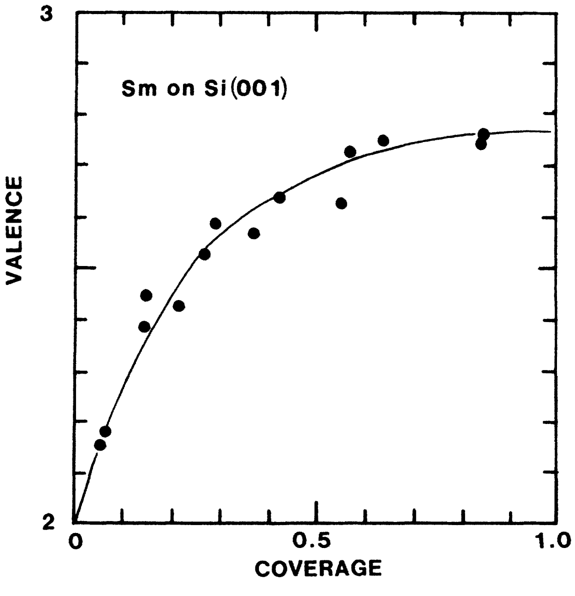

FIG. 2. The average valence as a function of Sm coverage with full coverage as unit (the line is drawn as a guide for the eye).

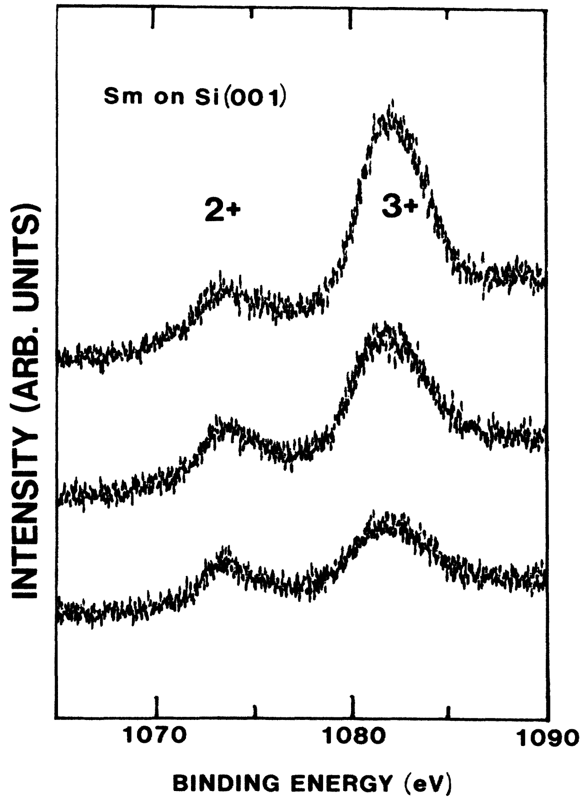

FIG. 3. The x-ray photoemission of the $3d_{5/2}$ lines for a Sm overlayer. The upper spectrum was recorded immediately after evaporation while the lower two spectra were recorded after annealing at 600 °C for two and four minutes, respectively.

ordered overlayers of Sm on Cu(001). For complete monolayers this is not necessarily surprising, because the average coordination and Sm-Sm separations would not differ greatly. These Sm interactions lead to a hybridized $6s$-$5d$ conduction band and the integrated density of states is insensitive to the degree of order.

At very low coverages, assuming the Sm atoms to be uniformly distributed over the surface, it might be thought that a substrate mediated Sm-Sm interaction (via Friedel oscillations in the substrate conduction band) is needed. Whereas this might be the case for a metallic substrate, it is inapplicable to semiconducting Si.

On the other hand, the free rare-earth atoms are very large, and one may ask what is the largest separation at which direct interaction (i.e., significant overlap of valence electron clouds) might arise. Using available data for the radial distribution functions for the Gd atom[17] (which has smaller diameter than the Sm atom), we set this upper limit at $\simeq 10$ Å. A hexagonal close-packed net with parameter 10 Å corresponds to a concentration 1.15×10^{14} atoms/cm^2. Converted to coverage, in the case of Sm/Cu(001), this gives $\theta = 0.074$. The point is that the lowest coverages studied by us for both Cu(001) and Si(001) substrates are of this size. In other words, it is highly probable that the variation of valence observed in our experiments is controlled wholly by direct Sm-Sm interactions. Even our most dilute overlayers lie within or at the threshold for such interactions. In this way we can account for the similarity between the Sm/Cu and Sm/Si systems. It is also clear that if the above explanation is correct it implies a weak Sm-substrate interaction; we may regard these Sm overlayers as good approximations to two-dimensional lattices of varying densities.

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