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Mixed valence in Sm overlayers on Al(001)

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Samarium is found to form ordered overlayers when deposited on a clean Al(001) substrate. Annealing is necessary to produce the crystallographic order. The x-ray photoemission spectrum from the $3d$ level of Sm in such layers shows that the occurrence of the divalent initial state is dependent on the presence of structural disorder or large separations between Sm atoms. In annealed structurally ordered films we find an average valence of 2.95 for the samarium atom. Spectroscopic data for the $3d$ levels are presented.

I. INTRODUCTION

As first pointed out by Wertheim and Campagna[1] the $3d$, $4d$, and valence-band x-ray photoemission spectra (XPS) of bulk Sm metal show that the atoms of Sm occur in both divalent ($4f^6$) and trivalent ($4f^5$) forms. In order to reconcile this situation with the conventional appreciation of Sm as a trivalent metal, Johansson[2] suggested that the divalent component is localized in the surface of the metal. Support for this proposal has been obtained through photoemission experiments which accentuate the contribution from the outermost surface layer.[3-6]

On the other hand, Mason *et al.*,[7] from a study of Sm films evaporated onto amorphous carbon, concluded that Sm clusters exhibit mixed valence which is sensitive to particle size; the Sm is primarily divalent for small cluster sizes ($\sim 30 \pm 10$ Å).

It seems that all photoemission studies have been made on evaporated films of Sm, most probably directly after evaporation and without subsequent annealing. As far as we are aware there is no information regarding the atomic surface of such evaporated films, yet any discussion of the valence of surface atoms in Sm, its homogeneity, or inhomogeneity must be hampered by the lack of information concerning the surface structure.

We feel that more knowledge on the intermediate valence of surface atoms of Sm might be obtained by the study of ordered overlayers of Sm formed on a well-characterized, clean, single-crystal substrate—if such layers can be formed. At the start of this work we were unaware of any study of adsorbed rare-earth elements on single-crystal substrates, but the data presented here show that ordered monolayers may be formed and lend themselves to study.

Assuming that an ordered monolayer of Sm may be obtained we chose Al(001) for the substrate. Aluminum is a nearly-free-electron metal, trivalent, and well characterized. The Sm $3d$ spectrum can be studied without any interference from that of the substrate.

We have in an earlier Communication concluded that in the ordered overlayers the Sm atom is trivalent.[8] The present data provide detailed confirmation of this conclusion. The structure of the overlayers, however, varies with thickness and is more complicated than originally thought. The occurrence of divalent Sm depended either on the presence of structural disorder in concentrated films or the wide separation of Sm atoms in dilute films. We consider our data to be characteristic of clean Sm overlayers.

II. EXPERIMENTAL TECHNIQUE

The apparatus used was a Vacuum Generators x-ray photoemission spectrometer fitted with a three-grid low-energy electron diffraction (LEED) unit and an argon-ion gun for cleaning purposes. The specimen could be cooled by liquid N_2 to close to $-100\,^{\circ}$C (as measured by a thermocouple). Normally during the course of an experiment the cooling was continuous, but the temperature of the specimen could be changed by heating the molybdenum foil on which the aluminum crystal was mounted. The specimen could be taken from -100 to $150\,^{\circ}$C in less than 3 min and recooled to below room temperature (RT) within 1 min. Prior to all measurements with Sm the Al crystal was cleaned by argon-ion bombardment (5 kV, ~ 50 μA) for periods of 15–30 min, depending on the amount of Sm to be removed from previous measurements. At the end of each bombardment the substrate was heated to $\sim 500\,^{\circ}$C and immediately cooled to below RT. This procedure gave sharp diffraction spots in LEED. A further check on the condition of the substrate was obtained by confirming the absence of both Sm and O_2 through their $3d$ and $1s$ spectra, respectively. Sm was evaporated from a closed tungsten basket which was heated by electron bombardment. The base pressure in our system was $< 5 \times 10^{-10}$ mbar and evaporation of a Sm film caused only a momentary increase to $\sim 2 \times 10^{-9}$ mbar.

XPS data were obtained using unmonochromatized Al $K\alpha_1\alpha_2$ radiation. Normally when studying the $3d$ spectrum the counting time was 615 s. When estimating valence from the integrated intensities of the $2+$ and $3+$ components of the $3d$ spectrum, allowance for the presence of $K\alpha_3\alpha_4$ satellite lines was always made.

III. STRUCTURE OF Sm LAYERS ON Al(001)

We found that Sm evaporated on the Al(001) surface at or below room temperature did not produce ordered monolayers nor ordered multilayers of Sm. Crystallographic ordering of such layers was obtained by rapid heating to ~150 °C. We have not as yet attempted to find the minimum temperature required to produce ordering.

The LEED patterns correspond to particular overlayer structures which were oriented parallel to either the [10] or [01] axes of the Al(001) surface. The patterns of Fig. 1 correspond to overlayer structures parallel to the [01] axis.

For very small deposits of Sm, much less than a monolayer, the annealed film showed, in LEED, continuous streaks parallel to the reciprocal net of the Al(001) surface. Further deposition and annealing led to the development of a discrete diffraction pattern with well-defined spots indicative of a superstructure [Fig. 1(a)]. Addition of more Sm caused the broadening or merging of certain reflections and the strengthening of others, introducing elements of sixfold symmetry [Fig. 1(b)]. As more Sm was put down the elements of sixfold symmetry became enhanced, but eventually the film, on annealing, became mechanically unstable and agglomerated, partially exposing the bare Al substrate. When a thick film was deposited cold it was possible to extinguish the Al $2p$ XPS signal completely; the Sm covered the whole substrate. However, on annealing, the Sm agglomerated and the Al $2p$ signal again became observable. Agglomeration resulted in a reduced Sm $3d$ signal presumably because of the formation of a thicker film with smaller total area. Normally a Sm LEED pattern was not observable after agglomeration, but on occasion we have obtained diffraction from patches of agglomerated Sm which showed round spots and sixfold symmetry.

The fact that for very small amounts of Sm the diffraction patterns showed continuous streaks parallel to the [10] and [01] axes indicated that the Sm atoms became aligned parallel to the rows of aluminum atoms in the surface layer, but as more Sm was deposited the pattern of Fig. 1(a) became particularly distinct; it is most conveniently described in terms of a centered rectangular reciprocal-lattice cell of dimensions $2\pi/6d$ and $2\pi/d$, d being the parameter of the Al(001) square net (2.86 Å). Such a reciprocal-lattice cell corresponds to a centered rectangular cell with dimensions $(12d,2d)$ in the direct lattice. We associate this diffraction pattern with the occurrence of coincidences in the arrangement of both Sm and Al atoms. Although the detailed arrangement of the Sm atoms must influence the diffraction pattern, the occurrence of the extra diffraction spots in Fig. 1(a), is, mainly, only dependent on the positions of coincidence. Thus several possible arrangements of the Sm atoms could have produced the observed LEED pattern. However, consideration of packing density and Sm nearest-neighbor distance leads us to speculate that the arrangement of Fig. 2 is a possible and probable overlayer structure. The unit cell of the Sm overlayer is taken to be of centered rectangular form and seven such cells are overlaid a (12×2) arrangement of Al unit cells. It is readily seen that this produces a $c(12\times2)$ coincidence net. The Sm coverage is $\Theta=0.58$ (where $\Theta=1$ corresponds to a [Sm]:[Al] ratio of 1) or a Sm-atom concentration of 7.3×10^{14} cm^{-2}. In such an overlayer each Sm atom has four nearest neighbors at a distance of 3.77 Å and two next-nearest neighbors at a distance of 4.91 Å. The latter separations may be compared with the interatomic separations in bulk Sm, namely, 3.629 and 3.587 Å.[9]

If we neglect the lenticular shape of certain diffraction spots, the pattern of Fig. 1(b) contains elements of hexagonal symmetry; the latter were found to become stronger with increasing Sm concentration. The progression from streaking at low Sm coverage through the patterns of Figs. 1(a) and 1(b) was a general feature of increasing Sm concentration.

We believe that these hexagonal features are to be associated with the formation of a second overlayer and speculate that the structure of this overlayer is as illustrated in Fig. 3. In the second layer of Sm the atomic separation along the [10] axis is taken to be the same as in the first overlayer; this separation determines the hexagonal cell parameter, 4.91 Å. This hexagonal overlayer forms a coincidence net with the underlying first overlayer, the coincidence cell being Sm$_1c(1\times3)$Sm$_2$, the subscripts referring to the two overlayers. In terms of the underlying Al(001) surface net this is almost, but not quite, identical to a coincidence net Al(7×3)Sm$_2$, as may be discerned from Fig. 2.

The occurrence of lenticular diffraction spots was a general feature of all the LEED patterns associated with more than one overlayer. A possible cause for their occurrence may be as follows. In the [10] direction the first

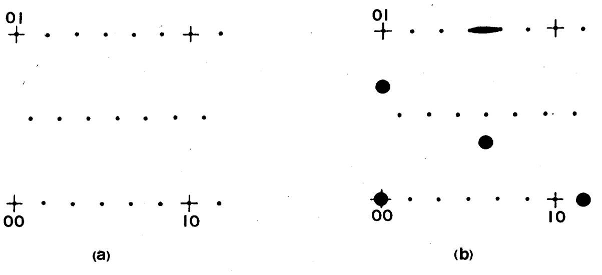

FIG. 1. LEED patterns observed from Sm overlayers on Al(001). Only spots arising from structures parallel to the [10] axis are shown for the first quadrant of the diffraction pattern. Al beams are denoted by +. Not all the diffraction spots were seen at the same time for a given beam energy. (a) Pattern arising from first complete overlayer. (b) Pattern arising when more than one overlayer present. The lenticular spot was a common feature of such patterns.

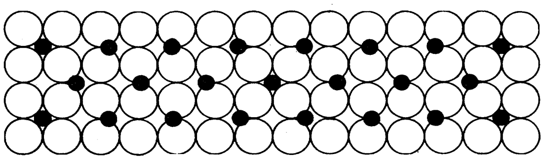

FIG. 2. Structure proposed for the first overlayer of Sm on Al(001) based on the LEED pattern of Fig. 1(a). The Al atoms are represented by the large open circles. Note that there is also a near, but not perfect, coincidence between four Sm separations and seven Al separations along the rows parallel to [10].

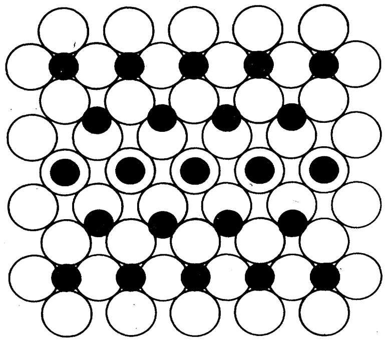

FIG. 3. Possible structure for a second overlayer of Sm. Here the first overlayer of Sm is represented by open circles, the scale being the same as in Fig. 2. The second overlayer as shown is almost perfectly hexagonal and based on a coincidence net of the form $\mathrm{Sm}_1(1\times 3)\mathrm{Sm}_2$ where the subscripts indicate first and second overlayers. The second overlayer also forms a not-quite-perfect coincidence net with the underlying Al substrate.

and second overlayers have the same interatomic spacing and the same coherence with the underlying Al(001) net. The "hexagonal" diffraction spot parallel to the [10] axis therefore coincides with a reflection from the $c(12\times 2)$ coincidence net between the substrate and the first overlayer, as well as the diffraction spot arising from the first overlayer. These overlapping diffraction beams produce the intense reflection at the position $(\frac{7}{6},0)$ in terms of the Al(001) reciprocal-net parameters. On the other hand, the off-axis hexagonal diffraction beam arising at the position $(\frac{7}{12},1)$ falls right between two reflections from the (12×2) coincidence net; all three beams merge to produce the broad lens-shaped diffraction spot.

Since the hexagonal aspects became accentuated with further increase in Sm concentration it is possible that a third layer, with structure similar to that of the second overlayer, also formed. The suggested structure for these hexagonal layers has lower packing than that for hexagonal layers in bulk Sm. We are unable to introduce denser packing without resorting to very large coincidence cells.

On the other hand, films thicker than about three overlayers were mechanically unstable and agglomerated on annealing, which indicates that the ordered films were probably very different from the bulk material. We do not know the structure of the agglomerated films although we might presume it to be that of ordinary Sm metal. After agglomeration LEED data were not usually obtainable, but occasionally we have observed truly hexagonal patterns with round diffraction spots and no features typical of Al(001). Nevertheless these patterns were otherwise very similar to those from the hexagonal overlayer indicating a parameter of ~4.7 Å; we are unable to reconcile this parameter with systems of hexagonal planes that arise in either bulk Sm or its known intermetallic compounds with Al.

IV. X-RAY PHOTOEMISSION RESULTS

The required information regarding the valence state of the Sm atom is provided by the $3d$ spectrum,[1,3] and $3d^{5/2}$

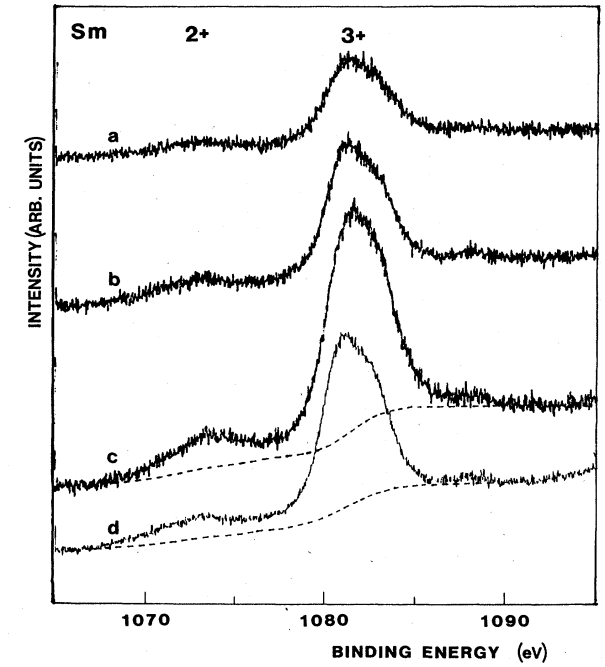

FIG. 4. Sm $3d^{5/2}$ core-line spectrum corresponding to different Sm coverages in the annealed condition. *a*, submonolayer coverage; *b*, approximately one monolayer; *c*, between one and two overlayers; *d*, approximately three overlayers. Data were taken under similar conditions and that for curve *d* has scale factor $\frac{1}{2}$ compared with the other curves. A hand-drawn background is illustrated in *c* and *d*. After allowance for the presence of $K\alpha_3\alpha_4$ satellites the average valency for the Sm in these films as estimated from the areas of the components is found to lie in the range 2.9–2.95.

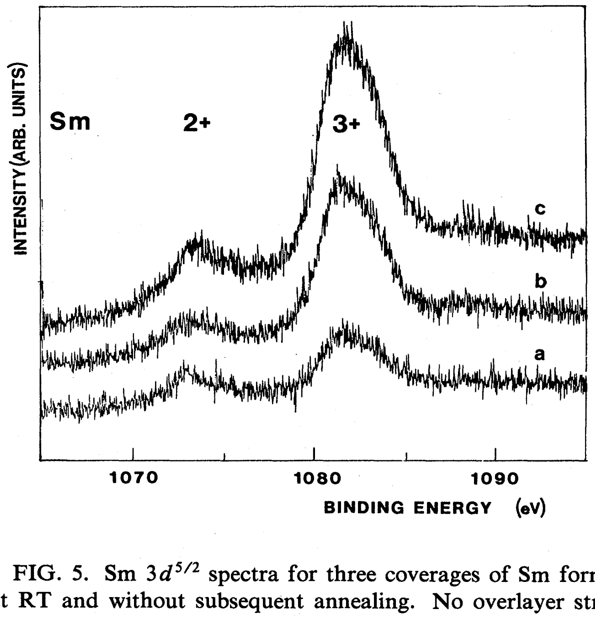

FIG. 5. Sm $3d^{5/2}$ spectra for three coverages of Sm formed at RT and without subsequent annealing. No overlayer structure was seen in LEED, but the Al reflections were clearly visible for conditions appropriate to curves *a* and *b* and were almost completely absent in curve *c*. The average valence lies in the range 2.8±0.05.

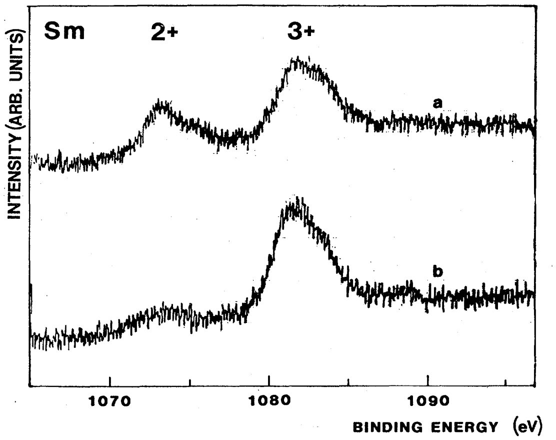

FIG. 6. Sm $3d^{5/2}$ spectrum for a disordered (curve *a*) and ordered (curve *b*) monolayer. The valency of the Sm atom is estimated to be 2.6 in the former and 2.9 in the latter condition. The Sm film was deposited at ~ -100 °C.

component with binding energy near 1081 eV being associated with the valence 3+ and the component near 1074 eV with the 2+ valence.

The calibration of the spectrometer was checked against the $2p$ spectra of both clean Al and Cu surfaces. The peak positions were found to arise at binding energies 72.9 and 932.8 eV, respectively, the spin-orbit splitting in Cu being 19.7 eV. These are in good agreement with accepted values[10] and the calibration is therefore considered reliable. In what follows we illustrate the influence of crystallographic order and coverage on the valence of the Sm atoms in the adsorbed layers.

Figure 4 shows the spectrum in the neighborhood of the Sm $3d^{5/2}$ line for four different ordered films taken under identical measuring conditions. The coverage varies from submonolayer concentration, curve *a*, through those typical of one and two overlayers, curves *b* and *c*, respectively, to that for an agglomerated film, curve *d*. Whereas for the first three overlayers the underlying Al LEED pattern was clearly visible, this was not the case for the patches which produced the data of curve *d*.

Spectra for three Sm films deposited and studied at room temperature are presented in Fig. 5. No overlayer structures were evident in LEED and whereas the Al(001) pattern was clearly visible in the films appropriate to curves *a* and *b* of this figure, it had almost disappeared for the film of curve *c*. These data were taken under different analyzer conditions to those of Fig. 4 and when allowance is made for the differences in signal strength the amounts of Sm deposited corresponded approximately to those which gave the spectra of curves *b*, *c*, and *d* in Fig. 4.

A single overlayer of Sm evaporated onto a cold substrate gave the spectrum of curve *a*, Fig. 6, whereas after annealing that shown in curve *b* was obtained. The complete $3d$ spectrum is exhibited in Fig. 7. The film in this case, when deposited and studied cold, completely extinguished both the Al LEED pattern and the Al $2p$ photoemission line; it gave rise to the spectrum Fig. 7, curve *a*. On annealing this film the Al $2p$ line again became observable. The $3d$ spectrum of this annealed film (Fig. 7, curve *b*) shows significant weakening of the 2+ component, but in addition new broad peaks have appeared on the high-binding-energy side of both $3d^{5/2}$ and $3d^{3/2}$ peaks.

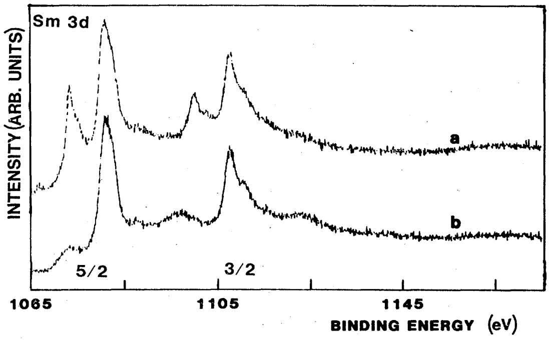

FIG. 7. Complete $3d$ spectrum for disordered (curve *a*) and agglomerated (curve *b*) films on Al(001). The Sm film was deposited at ~ -100 °C.

V. DISCUSSION

Allen *et al.*[4] have demonstrated that exposure to oxygen converts Sm to the 3+ state. It is therefore clear that the changes from the 2+ to the 3+ state could have been caused by oxygen contamination. However our monitoring of the 0 $1s$ line together with the fact that both the position and profile of the 3+ component of the $3d^{5/2}$ line were the same both before and after the valence transition (i.e., before and after annealing a given film) convince us that this was not the case. The changes observed did not arise as a result of contamination.

Our results for all annealed films, regardless of thickness, clearly show that structural order promoted the 3+ state. We have assessed the areas of the divalent and trivalent components of the Sm $3d^{5/2}$ spectrum and thereby estimated the average valence of the Sm atom. From the data of Fig. 5, after correction for the presence of $K\alpha_3\alpha_4$ satellites, we find an average valence of 2.95. The residual intensity in the neighborhood of the 2+ line in an annealed film was not due wholly to the $\alpha_3\alpha_4$ satellites from the 3+ component. The sharp peak in the 2+ line arises at 7 eV lower binding energy than the 3+ line, whereas the $\alpha_3\alpha_4$ satellites are a distance of 9.7 and 11.7 eV from the latter feature. Some remaining 2+ components in an annealed film may have arisen due to residual disorder, but it is more likely that it occurred because even if all the Sm atoms were initially in the trivalent condition the divalent state would arise as a final state. On this basis we conclude that for the films studied in this work the Sm was truly trivalent.

An indisputable result of the present work is that structurally disordered films, independent of thickness, always showed a larger proportion of Sm^{2+} than did annealed films. We also found more Sm^{2+} in films prepared at low temperature than in those prepared at RT, which is reasonable since colder substrates may be expected to produce greater disorder. It is also the case that we have, in unannealed films of submonolayer coverages, found the largest proportions of Sm^{2+}.[8] We do not know the structure of a disordered film but it is clear that when deposited onto Al(001) at or below RT there was little or no surface diffusion of Sm. Thus in such a film the Sm atoms were probably distributed essentially uniformly over the surface; at very low coverages this must have led to large Sm separations and weak Sm-Sm interactions, hence the large proportion of $2+$ in a dilute disordered overlayer. Our data imply that the isolated Sm atom on Al(001) was divalent and that the Sm-substrate interaction favored the $2+$ state.

If, on annealing, the Sm atoms, even at very low coverages, formed nuclei or islands of monolayer structure, then the Sm atom separations in annealed overlayers were always typical of complete overlayers; on this account there always arose Sm-Sm interactions which led to the $3+$ condition. The pronounced streaking observed in LEED patterns prior to the formation of proper diffraction spots supports such a picture. In this way we can understand the observation of the fully trivalent state in all the annealed films in spite of very different coverage. Unfortunately lack of absolute knowledge of the various structures arising in this system prevents a determination of the coordination and interatomic separation of the Sm atoms. We cannot decide whether the Sm-Sm interaction is a direct one or whether it is mediated by the substrate.

The occurrence of Sm^{2+} in ordinary evaporated films of Sm has been attributed to the narrowing of the conduction band for surface atoms, a direct result of reduced coordination in the surface layer.[3] The overlayers studied in the present work were not equivalent to bulk Sm; in all probability they were more dilute than the surface layer of bulk Sm, and band-narrowing effects should have been acute, particularly in a second or third overlayer when contact with the substrate was lost, but the Sm remained trivalent.

The agglomerated films are difficult to understand. One might have expected them to behave as bulk Sm metal or to reflect the properties of Sm clusters as described by Mason *et al.*,[7] but this was not the case; neither have we experimental evidence for the formation of any intermetallic compound.

The presence of the Sm might have caused some perturbation of the Al(001) surface electronic structure. However we found no shift in the position of the $2p$ core line of Al due to the presence of Sm. Using the LEED gun and the electron analyzer we studied the Al surface plasmons using electron-energy-loss spectroscopy. Primary electrons with energy ~60 eV were incident at a large angle of incidence ~75° and nonspecularly scattered electrons were collected in the analyzer assembly. This geometry favored excitation of surface plasmons and for the clean aluminum substrate we obtained a strong and sharp loss peak at 10.2 eV with a full width at half maximum (FWHM) of 3.3 eV. A double loss peak was also observed. Deposition of approximately one monolayer of Sm caused the disappearance of the double loss peak, a reduction in the number of inelastically scattered electrons relative to those elastically scattered, a slight increase in the width of the loss peak, but no significant change in its position. This trend increased with the thickness of the deposited Sm film. For an agglomerated film the inelastic peak was weak and broad (FWHM, ~6.5 eV) and centered at 11 eV.

Returning to the $3d^{5/2}$ spectrum we note in the spectrum from a single overlayer, but more particularly so in thicker films, in both disorderd and annealed conditions an extra weak feature on the high-binding-energy side of the main line; it arises at 1088 eV, being 6.6 eV from the main peak. This extra line was present in all but the weakest spectra; it can be seen in the data of Figs. 4–7. We tentatively associate it with a $4f^4$ final state. Its $3d^{3/2}$ counterpart is not distinguishable in the long tail to the Sm $3d^{3/2}$ line.

Comparing the spectra of Fig. 7 we note the presence of new broad peaks in the annealed film. These extra peaks became more apparent with increasing thickness and were always seen in agglomerated films. They are located with their maxima ~15.5 eV on the high-binding-energy side of the main lines. We believe these extra peaks are due to the extrinsic excitation of substrate bulk plasmons.

It will be noted that the spectra presented here show no well-defined inelastic peaks arising from the Sm overlayers. We also searched for such losses using electron-energy-loss spectroscopy but none were seen.

VI. CONCLUSIONS

Our experiments have shown that overlayers of Sm with crystallographically ordered structures can be formed on an Al(001) surface. Sm films formed at RT or below were not structurally ordered. Regardless of the amount of Sm deposited we have always observed a conversion to the $3+$ state as a result of annealing and structural ordering. Moreover, the behavior was independent of thickness. We believe the Sm existed wholly in the $3+$ state in the annealed films.

We conclude that the isolated Sm atom on Al(001) was divalent but Sm-Sm interaction favored the trivalent condition. The conversion to the $3+$ state on annealing, even at very low coverages, arose because the first overlayer grew by the formation of separate nuclei leading to Sm-atom separations which were essentially independent of coverage in the annealed film.

From measurements taken in the course of the present work we provide the following spectroscopic data for Sm deposited on Al(001).

	Binding energy (eV)		
	$3d^{5/2}$	$3d^{3/2}$	
Sm^{2+}	1073.6±0.2	1100.7±0.2	
Sm^{3+}	1081.2±0.2	1108.2±0.2 1111.3±0.2	multiplet

Our spectroscopic data have also revealed a weak component at 1088 eV which we tentatively associate with a Sm^{4+} $(4f^4)$ $3d^{5/2}$ excited state. The above data are for agglomerated films; in true surface overlayers the electron binding energies were shifted ~0.2 eV to higher values.

ACKNOWLEDGMENTS

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[1] G. K. Wertheim and M. Campagna, Chem. Phys. Lett. **47**, 182 (1977).

[2] B. Johansson, Phys. Rev. B **19**, 6615 (1978).

[3] G. K. Wertheim and G. Crecelius, Phys. Rev. Lett. **40**, 813 (1978).

[4] J. W. Allen, L. I. Johansson, I. Lindau, and S. B. M. Hagström, Phys. Rev. B **21**, 1335 (1980).

[5] J. K. Lang and Y. Baer, Solid State Commun. **31**, 945 (1979).

[6] A. Rosengren and B. Johansson, Phys. Rev. B **26**, 3068 (1982).

[7] M. G. Mason, S. T. Lee, G. Apai, R. F. Davis, D. A. Shirley, A. Franciosi, and J. H. Weaver, Phys. Rev. Lett. **47**, 730 (1981).

[8] Å. Fäldt and H. P. Myers, Solid State Commun. **48**, 253 (1983).

[9] F. H. Ellinger and W. H. Zachariasen, J. Am. Chem. Soc. **75**, 5650 (1953).

[10] *Photoemission in Solids I,* Vol. 26 of *Topics in Applied Physics,* edited by M. Cardona and L. Ley (Springer, Heidelberg, 1978), p. 265.