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Homogeneous intermediate valence of Sm on Al(111)

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Ordered and disordered monolayers and submonolayers of Sm were formed on Al(111). The ordered monolayer has the structure Al(2×2)Sm. Valence-band and Sm $3d$ core-level photoemission spectra were taken using Al $K\alpha$ radiation. The data show that the $3d$ core spectrum is a true replicate spectrum and allows a measurement of the valence. Sm in ordered overlayers always exhibited a valence of 3, whereas in disordered overlayers the Sm atom presented a valence of 2.4 at very low coverage, rising to a value of 2.8 at multilayer coverage. It is argued that the measured valence for the disordered submonolayer is site independent and homogeneous. The interaction with the aluminum substrate is sufficient to promote intermediate valence in the isolated adsorbed Sm atom, leading to a valence of 2.4.

I. INTRODUCTION

In spite of the intense interest in the physical properties of the rare-earth metals, their alloys and compounds, well characterized overlayers of rare-earth metals on single crystal substrates have received very little attention. Yet the quasi-two-dimensional character of monolayers may cause them to exhibit properties complementary to those of conventional bulk samples. This is probably particularly true in the case of the intermediate valence of Sm metal. In what follows we shall use the term intermediate valence to mean homogeneous non integral valence; the atom is imagined as existing in a mixture of two electron configurations. In the case of Sm these configurations are $4f^6(5d,6s)^2$ and $4f^5(5d,6s)^3$ which we shall also refer to as the 2 + and 3 + valence states, respectively.

The initial suggestion[1,2] that Sm exhibited intermediate valence was based on core-level and valence-band spectra obtained with ordinary evaporated films using x-ray photoelectron spectroscopy. Since the properties of bulk Sm indicate a $4f^5$ configuration it was suggested that the atoms in the intermediate-valence, alternatively wholly divalent state, are confined to the surface layers.[3,4] In the light of XPS and bremsstrahlung isochromat spectroscopy (BIS) Lang and Baer[5] concluded that the surface atoms are divalent. In fully coordinated bulk Sm BIS data show that the $4f^6(5d,6s)^2$ configuration lies 0.46 eV above the Fermi level E_f. This conclusion has been corroborated recently in photoemission experiments with synchrotron radiation, Gerken *et al.*[6] The latter authors, again using conventional evaporated films, show that in the rare earth metals the $4f$ final-state multiplets arise as "doublets," a result of photoelectrons which originate in the atoms in the surface layer having slightly larger (~0.5 eV) binding energies than those leaving the atoms within the bulk of the sample. For Sm, however, the characteristic final-state multiplets associated with the initial $4f^5$ and $4f^6$ configurations do not show this doubling effect because the $4f^5$ initial-state configuration arises only in the bulk and the $4f^6$ only on the surface. As originally suggested[5] the occurrence of divalent Sm in the surface atoms is therefore due to a "surface shift" which brings the $4f^6$ configuration below E_f. This means that in conventional bulk films Sm metal does not exhibit intermediate valence, but a limiting form of site-dependent valence. One might therefore be tempted to conclude that any two-dimensional arrangement of Sm atoms would be divalent, but this, as we shall show, is not the case and Sm overlayers on different single-crystal substrates present a wide variation of valence.

Our approach has been to use the $3d^{5/2}$ spectrum to assess the valence of Sm atoms in thin films corresponding to coverages varying from less than 0.1 monolayer to several overlayers, but our conclusions are based only on data for overlayers with coverage $\Theta \leq 0.5$ (coverage 1 being equivalent to one Sm atom to every substrate surface atom). In earlier work[7–9] we have studied both disordered and ordered overlayers of Sm on Al(001), Cu(001), and Si(001) surfaces. In the case of Sm on Cu(001) (Ref. 8) there is no dependence of the behavior of Sm on crystallographic order. For the first fully developed monolayer, which has structure Cu$(\sqrt{5}\times\sqrt{5})R(\pm 26.6°)$Sm, sites are necessarily similar and the measured valence 2.5. The variation of valence with coverage for both ordered and disordered overlayers implies that the isolated Sm atom on Cu(001) has valence 2, whereas for $\theta > 0.5$ the valence saturates at 2.75. These results clearly demonstrate that the valence of the Sm atom under these conditions is not site dependent. In the case of the Si(001) (Ref. 9) substrate only disordered overlayers could be formed; the variation of valence with coverage was very similar to that observed with the Cu substrate, yet the electronic and crystallographic nature of the substrate surface was very different. This again points to an insensitivity to crystallographic site. The first monolayer of Sm to form on Al(001) has a coincidence structure Al$c(12\times 2)$Sm with probable coverage $\theta = 0.587$. Although we cannot be certain of the exact arrangement of Sm atoms in the overlayer they must occupy nonequivalent surface sites, yet the $3d^{5/2}$ core spectrum (neglecting possible very weak satellite structure) indicates the valence 3 + . In the case of the Al(001) substrate the annealed overlayers always show a valence 3 + independent of coverage, but the disordered overlayer exhibits intermediate valence. We have earlier argued[7] that this is most likely due to island growth of the overlayer. Due to an accident with the Al(001) substrate we were unable to study disordered overlayers in detail, but tentatively concluded that the isolated Sm atom on Al has valence $2+$. The data presented in this paper will show that the above conclusion is incorrect.

Assuming that the $3d^{5/2}$ spectrum provides a correct measure of the valence of the Sm atom our earlier results[7-9] are in favor of a site-independent valence, i.e., a true homogeneous intermediate valence.

Nevertheless the use of the $3d$ spectrum to assess the valence of Sm is open to criticism because a replicate spectrum originating from a configurationally mixed initial state is indistinguishable from a satellite spectrum arising from Sm atoms in a single initial state ($4f^5$) but which have available two final states, in this case the $4f^5$ and $4f^6$ configurations.[10,11] We have earlier argued in favor of the replicate spectrum.[9]

Satellite spectra are caused by final states with different f counts. They are not expected to arise in the $4f$ spectrum[12] and no evidence for their occurrence in any rare-earth metal is available.[5,6] Thus it is desirable to vindicate the use of the $3d^{5/2}$ spectrum by obtaining valence-band spectra demonstrating the presence of the initial $4f^6$ configuration. The valence-band spectrum is much more difficult to obtain than the $3d$ spectrum on account of a lower ionization cross section for the $4f$ electrons; furthermore any evaluation of the valence (which we have not attempted to do) demands a very high resolution. These difficulties are aggravated when the sample is only a fraction of a monolayer and when the substrate itself has a pronounced valence-band spectrum as is the case for Cu and Si, but the valence band for Al is essentially featureless.

Our object therefore with the present paper is to present $3d$ and valence-band spectra for Sm overlayers on Al(111) and to demonstrate the replicate character of the $3d$ spectrum. We shall also show that the data obtained indicate that the isolated Sm atom on Al(111) has valence 2.4, i.e., the interaction with the aluminum substrate is itself sufficient to produce intermediate valence in the isolated Sm atom. The data presented are considered 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 ion gun for cleaning purpose. The experimental procedure was the same as described previously.[7] The base pressure in the system has been improved to be $\leq 10^{-10}$ mbar and certain changes in data accumulation procedures have been made. Spectra were taken with unmonochromatized Al $K\alpha$ radiation and they are presented as recorded without any subsequent treatment. When estimating valence from the integrated intensities of the $2+$ and $3+$ components of the $3d^{5/2}$ spectrum correction for the presence of $\alpha_3\alpha_4$ satellites is made. The use of unfiltered Al $K\alpha$ radiation severely limited the resolution obtainable. We have therefore taken a certain amount of data using HeII radiation particularly to demonstrate presence of the $4f^5$ final-state multiplet originating from the $4f^6$ initial state.

III. STRUCTURE OF Sm LAYERS ON Al(111)

Sm evaporated onto an Al(111) surface at or below room temperature did not form ordered monolayers nor ordered multilayers. We observed an Al(2×2)Sm overlayer when Sm was evaporated onto a warm ($\sim 150°$C) substrate. This was the only overlayer structure observed.

No LEED pattern was seen when the substrate was covered by more than approximately two to three monolayers of disordered Sm. As previously observed with an Al(001) substrate, uniformly thick disordered Sm films deposited at $\sim -100°$C agglomerated on annealing to produce thicker regions of Sm and patches of uncovered Al(111) substrate.

IV. PHOTOEMISSION RESULTS

As for Sm on Al(001) it was established that for all the coverages used in this work the ordered (annealed) overlayers contained only $3+$ Sm. Interest was directed primarily to disordered overlayers formed by evaporation onto the cold substrate. The practice was therefore to deposit Sm onto the cold substrate and determine the Sm $3d^{5/2}$, Al $2p$, and valence-band spectra in this order; thereafter the sample was annealed, recooled, and either $3d^{5/2}$ or valence-band spectrum remeasured. The $3d^{5/2}$ spectrum may be used as a measure of coverage; this measure is linear only for low coverages and with the aid of LEED data conversion to true coverage can be made.

It was a straightforward matter to obtain data for the $3d^{5/2}$ spectrum in both disordered and ordered forms because the counting time in all but the most dilute films was only approximately 4 min per spectrum. The valence-band spectrum presented greater difficulty and counting times varied from $\sim$17–70 min. Unlike work with thick polycrystalline films it was not possible to renew a contaminated sample by evaporation of further material and a compromise between counting time and counting statistics had to be made. In all the data to be presented there is no significant effect of contamination. The greatest difficulty was experienced with the He resonance lamp. The He II intensity was very low and variable.

In Figs. 1–4 we present both valence-band and $3d^{5/2}$ spectra for disordered Sm overlayers of different coverages. The valence-band spectra appropriate to the annealed or ordered states for all but the thinnest films are also shown. For the two most dilute overlayers we have also corrected the valence-band spectrum for the contribution from the substrate and in proportion to the strength of the Al $2p$ signal. The valence of the Sm in disordered overlayers was calculated from the integrated intensities of the two components of the $3d^{5/2}$ replicate spectrum allowance for the $\alpha_3\alpha_4$ satellites being made. This valence is, in Fig. 5, plotted as a function of the total integrated $3d^{5/2}$ spectrum. The region of coverage where, in the annealed state, an Al(2×2)Sm LEED structure was seen is also marked in this figure. A fully developed such overlayer corresponds to a coverage 0.25; we therefore normal-

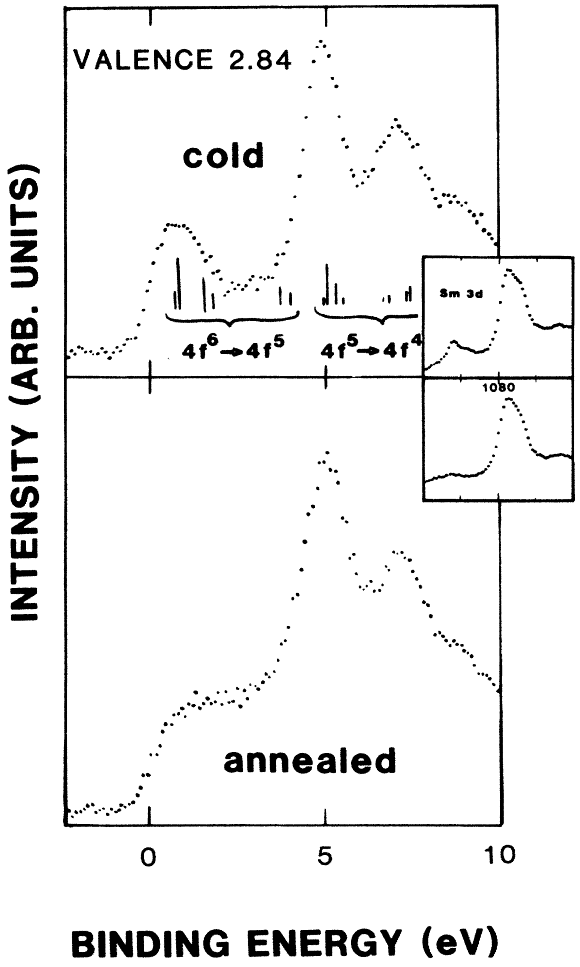

FIG. 1. Valence band and $3d^{5/2}$ spectra for a disordered and ordered Sm overlayer of coverage greater than 1. The valence determined from the $3d$ spectrum is 2.84.

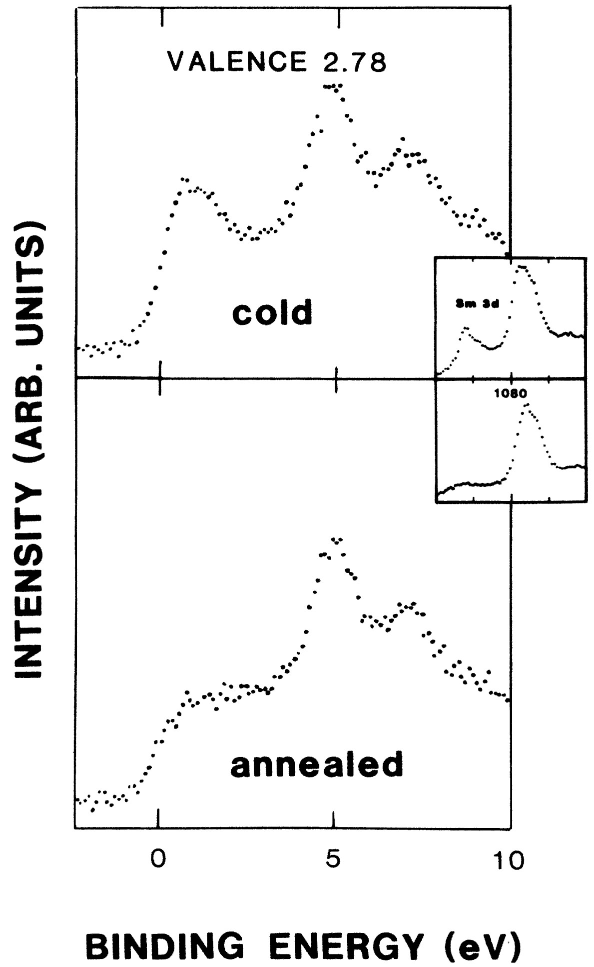

FIG. 2. Valence band and $3d^{5/2}$ spectra for a disordered and ordered Sm overlayer of coverage ~1. The valence determined from the $3d$ spectrum is 2.78.

ize the coverage scale so that this value of 0.25 is associated with the midpoint of the range where the LEED overlayer pattern was seen. Figure 5 clearly shows that for the limiting condition of infinitely small coverage the Sm atom on Al(111) exhibits a valence of 2.4.

V. DISCUSSION

The final-state multiplets arising from the initial $4f^5$ and $4f^6$ configurations have been described in detail;[13,14] (we indicate the positions and relative intensities of the components of each multiplet in Fig. 1). With the resolution available [full width at half maximum (FWHM) = 0.7 eV] the $4f^5$ final state multiplet is not resolved in the x-ray spectrum. Nevertheless the difference in intensity near 1 eV in the spectra of disordered and ordered overlayers is clearly marked and presented at all coverages; furthermore we see, admittedly only qualitatively, that its relative strength follows that of the 2+ component of the $3d^{5/2}$ spectrum. In order better to demonstrate the true presence of the $4f^5$ final-state multiplet we show in Fig. 6 valence-band spectra taken with He II radiation (photon energy 40.8 eV) for two disordered films of different cov-

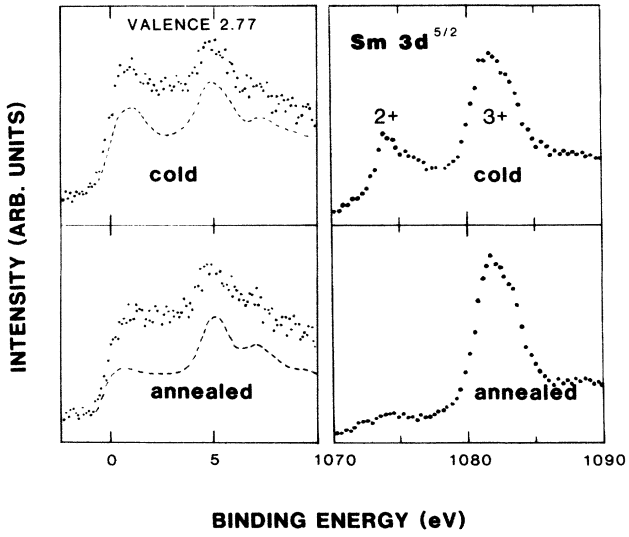

FIG. 3. Valence band and $3d^{5/2}$ spectra for an overlayer of coverage 0.35 in both the disordered, and ordered states. The dashed lines indicate the valence spectrum corrected for the substrate contribution. The valence determined from the $3d$ spectrum is 2.77.

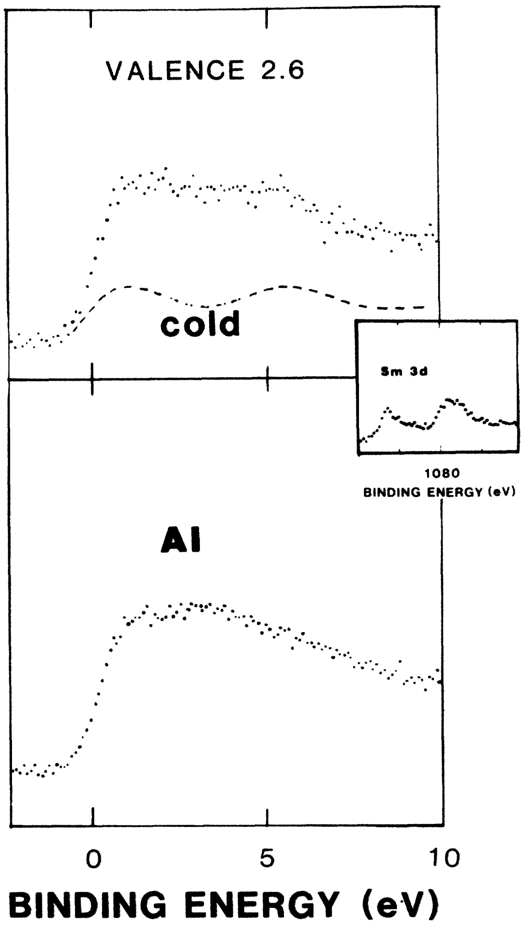

FIG. 4. Valence band and $3d^{5/2}$ spectra for a disordered Sm overlayer of coverage less than 0.1 together with the valence band of the clean Al(111) substrate. The valence determined from the $3d$ spectrum is 2.6.

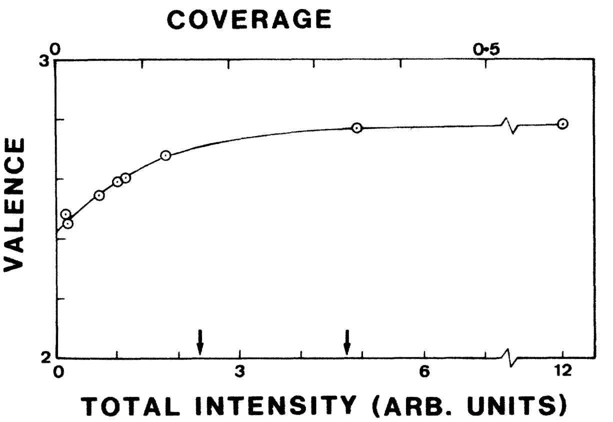

FIG. 5. The valence of Sm, as determined from the $3d^{5/2}$ spectrum, in disordered overlayers as a function of coverage. The arrows indicate the limits of integrated intensity within which and Al(2×2) Sm overlayer structure was seen in annealed overlayers. This observation provides the coverage scale in the upper abscissa.

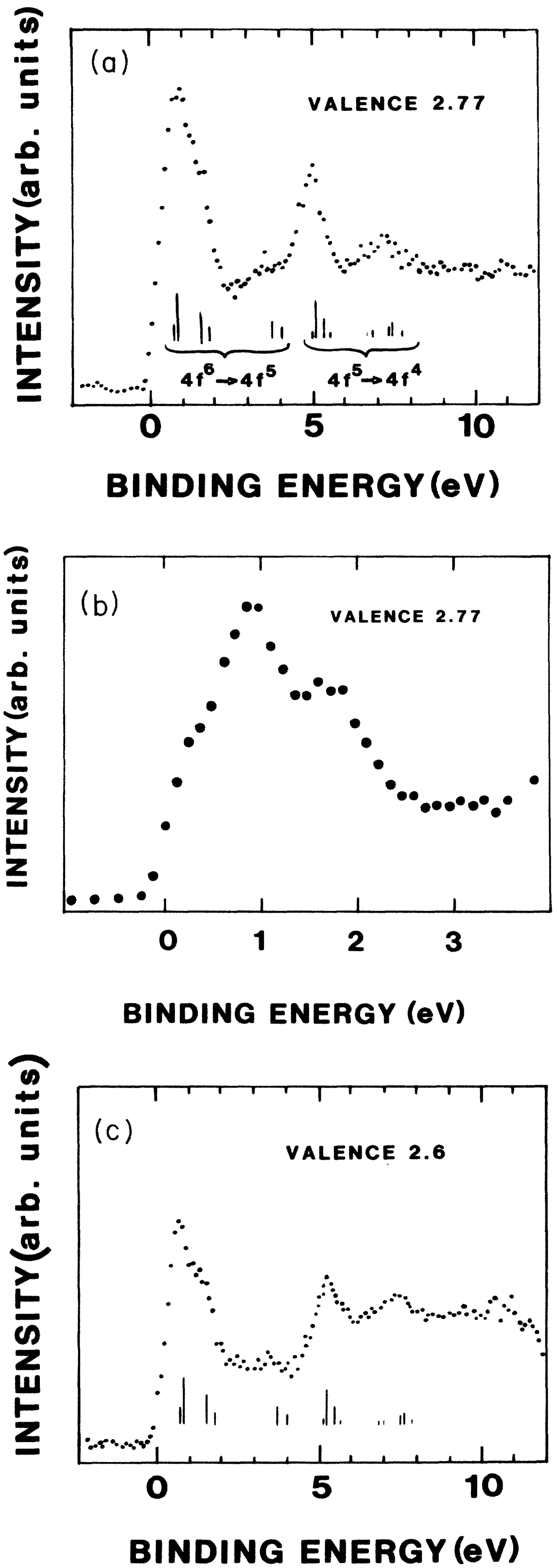

FIG. 6. Valence-band spectra taken with He II radiation. (a) Disordered Sm film several overlayers thick, valence according to $3d$ spectrum 2.77. Resolution (FWHM) ~0.4 eV. (b) Detail of previous spectrum at improved resolution ~0.25 eV. (c) Disordered Sm film of submonolayer coverage, valence according to $3d$ spectrum 2.6. Resolution ~0.4 eV.

erage and valence. The total resolution in this instance is equivalent to a FWHM ≈ 0.35 eV. The components of the $4f^5$ final-state multiplet are clearly indicated. We have used greater resolution to resolve fully this multiplet structure, but at considerable loss of signal strength so that the spectral range was limited to 1.5 eV.

In the ordered state this multiplet structure is absent. We therefore conclude that the $3d$ spectrum is a true replicate spectrum and permits proper measure of the intermediate valence.

Recalling our earlier discussion of the site dependence of the valence in Sec. I we believe the experimental data presented here (as well as data obtained earlier[7–9]) provides evidence for the homogeneous intermediate valence of Sm in the overlayers.

A necessary condition for this conclusion is that the monolayer and submonolayers are truly composed of isolated atoms and that atomic clusters do not occur. We believe that this is the case. The amount of Sm deposited in the case of an overlayer with $\theta = 0.25$ is one Sm atom to every four substrate atoms. The average separation is $\approx 2r$ where r is the substrate parameter (2.8 Å). At $\theta \approx 0.1$ the average separation becomes greater than $3r$. If clusters are to form at these low coverages diffusion over several atom spacings is needed; furthermore the probability for cluster formation must diminish with decreasing coverage. The massive substrate at a temperature less than -100°C is an effective sink for the thermal energy of the impinging atom and its diffusion on the surface must be severely limited. If diffusion arises we expect the Sm atoms, rather than form clusters, to occupy crystallographically prefered sites since the ordered structure is the equilibrium form for the monolayer or submonolayer. It is self contradictory to suppose that impinging Sm atoms first diffuse to form clusters which at a later time dissociate and the atoms again diffuse to form an ordered overlayer.

If clusters form we expect them to have very little influence on the sharpness of the LEED pattern arising from the substrate, but in fact in the presence of a disordered overlayer the substrate LEED pattern became diffuse, the moreso the greater the coverage. Clusters of Sm have been observed on graphite,[15] but the results of such work have little or no bearing on the experiments discussed here; graphite is a substrate usually chosen for the express purpose of promoting cluster formation.

Returning to Fig. 5, and in the light of the previous discussion, we conclude that the isolated Sm atom on the Al(111) surface has intermediate valence 2.4, which is to be contrasted with the valence 2 for the isolated atom on Cu(001) and Si(001). The intermediate valent state is a result of a many body interaction involving $4f$ core levels and itinerant valence states[16] leading to the degeneracy of two-electron configurations. The density of itinerant states must clearly be a significant factor. In the case of the isolated Sm atom on a metallic substrate, the latter controls the position of the Fermi level, the density of states at the Fermi level and the conduction-band breadth. The valence electrons of the adsorbed atom must accommodate themselves to the substrate band structure in a manner similar to the conventional dilute solid solution. We expect the many-body interaction promoting the intermediate valent state to be stronger the greater the substrate bandbreadth and the greater the density of states at the Fermi level. The free atom of Sm is divalent; we conclude that the Si and Cu substrates have insufficient surface and density of electron states significantly to perturb the stability of the divalent configuration of the Sm atom. Aluminum, on the other hand, has a denser electron gas than bulk Sm, the plasmon energy of Al being 15.5 eV compared to ~ 12 eV for Sm. The band breadth is also larger in Al than Sm. We suggest that these conditions suffice to promote an intermediate valence of 2.4 in the adsorbed atom. In similar fashion we explain the valence of 3 found in the ordered monolayers on Al compared with the value of 2.75 for Sm on Cu.

The variation of valence with increasing coverage for $\theta > 0.05$ is associated with the formation of a Sm surface band structure via direct Sm-Sm interactions.[9] We have no information regarding the initial variation of valence at very low coverages, but one may presume the presence of substrate-mediated indirect Sm-Sm interactions for the metallic substrates. Such a mechanism is inapplicable to Si and one might therefore conjecture that at very small coverages all the adsorbed Sm atoms are divalent until a critical coverage for direct Sm-Sm interaction is obtained.

Aluminum is the archetype of the simple metal or "pseudoatom" with a small ion core and almost uniform electron gas; its surface presents an approximately uniform planar distribution of electronic charge.[17] It is not surprising therefore that the Sm valence is so insensitive to occupation site, or that we find no difference in the behavior of Sm on Al(001) and Al(111). In all probability the same behavior would be found on a coarse-grained polycrystalline Al substrate. If, in this connection, we attach little significance to the Cud states we may assume a similar situation for the Cu and Si substrates.

The above discussion is limited to overlayers with coverage $\theta \leq 0.5$. As more Sm is deposited we enter the region of the very thin evaporated film ($\approx 3-10$ monolayers) and one might expect to find a Sm valence similar to that found with ordinary evaporated films. For the Cu and Si substrates this is the case, but for the Al substrate the annealed films always exhibit the valence 3. We are unable to explain this result. For the ordered monolayers which give rise to well-defined LEED patterns we can exclude the possibility of alloying of the Sm with the substrate.[7] For the thicker films LEED patterns are not observed, we can neither prove nor disprove an alloying interaction; we find however no chemical shift of the Sm $3d$ and Al $2p$ levels.

VI. CONCLUSIONS

(i) The $3d$ spectrum of Sm adsorbed onto Al(111) is a true replicate spectrum reflecting a distribution of initial states.

(ii) The isolated Sm atom adsorbed onto Al(111) has intermediate valence 2.4.

(iii) Sm forms an ordered (2×2) monolayer on Al(111). The valence in this monolayer is 3.

(iv) The valence of Sm adsorbed on Al(001), Al(111), Cu(001), and Si(001) is site independent.

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