

Valence-Transition-Induced 5×5 Surface Reconstruction of Sm(0001)

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Single-crystal Sm(0001) surfaces have been grown epitaxially on Mo(110). At low temperatures LEED shows a 5×5 surface reconstruction. This new type of valence-transition-induced reconstruction corresponds to a 25% expansion of the interatomic distances in the topmost hexagonal surface layer. At room temperature the 5×5 LEED pattern disappears due to a disordering of the surface. This suggests a very low melting temperature for the surface which may have implications for the understanding of the anomalous melting temperature of Sm metal.

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Detailed knowledge of the surface structure is of fundamental importance for the microscopic understanding of surface properties of solids. This explains the large experimental and theoretical activity in the field of surface crystallography. The pure metals have been extensively investigated in this respect. It seems to be a general phenomenon that the interlayer spacings are modified close to the surface (relaxation). In a few cases the influence of the surface is large enough to cause reconstruction.^{1,2} In general, this occurs for relatively open surfaces which by reconstruction become more closely packed, thereby reducing the number of "dangling bonds." The (110) surfaces of the fcc (face-centered cubic) metals Ir, Pt, and Au reconstruct by forming (111)-like microfacets.³ The (100) surfaces of the same metals reconstruct with somewhat disordered close-packed hexagonal overlayers.⁴ The reconstruction of the (100) surfaces of the bcc (body-centered cubic) metals W and Mo is interpreted as a chain formation of the surface atoms.⁵ This reconstruction seems to be removed at higher temperatures due to disordering effects. Au(111) is the only close-packed surface which has been found to reconstruct. This reconstruction is of a rather complex nature ($\approx \sqrt{3} \times 22$) and involves a 4.5% contraction of the surface atoms along one of the (110) directions.⁴

Sm is a metal with very special surface properties. The bulk metal has a $4f^5[5d5s]^3$ (trivalent) configuration. The $4f$ electrons are corelike while the $5d$ and $6s$ valence electrons take part in the bonding of the metal. Photoemission has shown that the surface atoms have a $4f^6[5d6s]^2$ (divalent) configuration;⁶⁻⁹ i.e., one of the bonding electrons has been incorporated in the localized $4f$ shell. It has been speculated that this difference in valence electronic structure could have drastic consequences for the surface structure. It can, for instance, be estimated that the equilibrium radius of a divalent Sm atom is 15% larger than that of a trivalent one.¹⁰ The divalent surface layer is therefore expected to be expanded relative to the bulk. Experimental evidence for such

surface effects has been lacking because of the difficulty in preparing clean single-crystalline surfaces of Sm.

In this Letter we show that the surface valence transition of Sm indeed causes reconstruction. Single-crystal surfaces of Sm have been obtained by epitaxial growth. The close-packed (0001) surface of Sm shows a 5×5 LEED (low-energy electron diffraction) pattern. A structural model for the reconstructed surface is proposed. Photoemission measurements are used to determine the amount of surface atoms in the reconstructed phase and the results are fully consistent with the model. The reconstruction is only seen at low temperatures. The surface layer disorders easily and at room temperature the 5×5 LEED pattern has disappeared. This order-disorder transition is reversible. This suggests that the Sm surface melts already at very low temperatures.

Sm single-crystal surfaces were grown on a Mo(110) substrate at room temperature (RT). The measurements were performed either at RT or at 80 K. Sm grows with the close-packed (0001) layers parallel to the Mo surface¹¹ and the growth mode is essentially of a layer-by-layer type.¹² Sm has a complex bulk crystal structure with a combination of fcc and hcp stacking sequences. The depositions were monitored by LEED, AES (Auger electron spectroscopy), work-function measurements, and photoemission at the MAX synchrotron-radiation laboratory in Lund. The films were many layers thick [> 6 monolayers (ML)] and no signal from the substrate could be detected by AES or photoemission.

Figure 1(a) shows the LEED pattern from a thick Sm film at 80 K. It is directly seen that the pattern is characteristic of an $n \times n$ reconstructed hexagonal surface. In Fig. 1(b) a schematic picture of the pattern is shown. From the pattern it is not immediately obvious which spots should be identified as substrate spots. However, by utilizing the LEED pattern of the clean Mo(110) substrate it was found that the spots marked as open squares in Fig. 1(b) are compatible with a close-packed trivalent Sm(0001) layer¹¹ in terms of both orientation and reciprocal-lattice spacings. The recon-

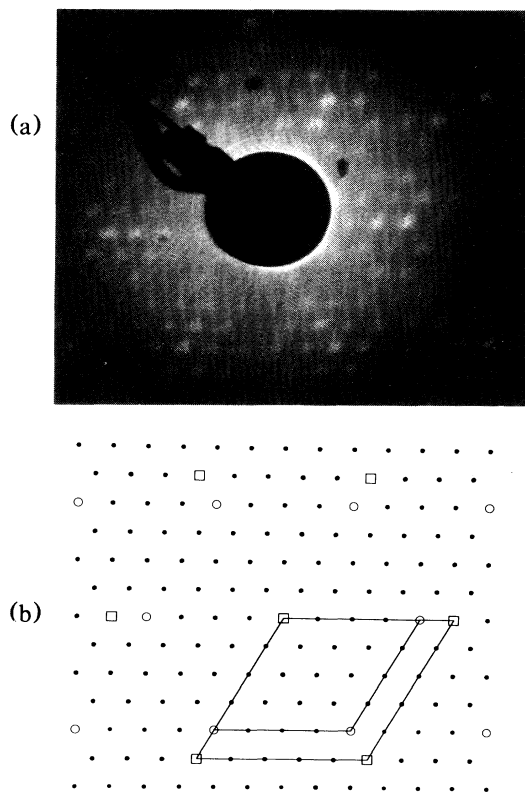


FIG. 1. (a) Photograph of a LEED pattern from the 5×5 reconstructed $\text{Sm}(0001)$ surface and (b) corresponding schematic picture.

struction is thereby identified as 5×5 . A general property of the pattern is that the overlayer spots marked with open circles in Fig. 1(b) are considerably stronger than the rest. These spots can therefore be interpreted as single-scattering spots from a hexagonal overlayer which is expanded (but nonrotated) relative to the bulk. (Single-scattering spots are those which should be the only ones present in a diffraction pattern from a hypothetical sole atomic layer. It is likely that these spots also are strong in the presence of a substrate.¹³) The rest of the spots in the 5×5 pattern are due to double diffraction between this expanded overlayer and the bulk.

Based on the LEED results we propose the surface structure in Fig. 2. The surface layer is obtained by expanding the bulk interatomic distances by 25%. The basic reason for this expansion is the surface valence transition to be the divalent state. Note, however, that the surface does not correspond to a fully contracted divalent layer. This is immediately seen from Fig. 2. The surface atoms have been drawn with the characteristic Sm^{2+} radius, and it is clearly seen that there is a considerable further expansion of the surface layer. The surface atomic density in the proposed structure is only 0.64

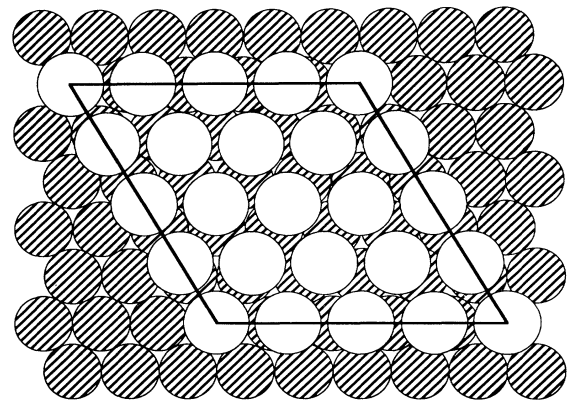


FIG. 2. The proposed 5×5 reconstructed surface structure. Striped circles represent the bulk (trivalent) atoms and open circles represent the surface (divalent) ones. The open circles are drawn according to the expected divalent radius.

relative to a close-packed $\text{Sm}(0001)$ bulk plane while a fully contracted surface layer would have a density of 0.76.

A critical test for the proposed structural model would be to have an independent measure of the absolute amount of divalent Sm . Such a measure can be obtained by carefully monitoring the growth of the Sm film by photoemission. The photoemission spectrum of a thick epitaxial Sm layer is shown in Fig. 3. As can be seen, the spectral features belonging to Sm^{2+} and Sm^{3+} are

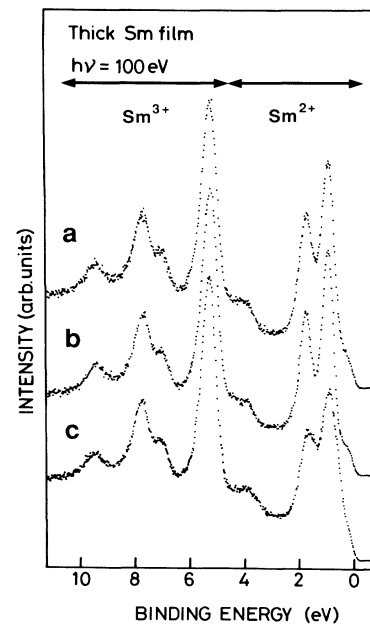


FIG. 3. Photoemission spectra from thick evaporated films of Sm . (a) A spectrum from a film deposited and measured at RT; (b) a spectrum from the same film but measured at 80 K. (c) A spectrum from a film deposited and measured at 80 K.

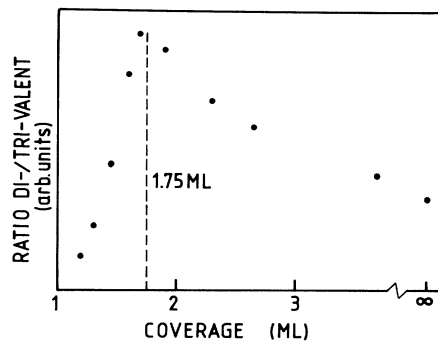


FIG. 4. The intensity ratio between divalent and trivalent Sm signals as a function of Sm coverage. The maximum is reached between 1.70 and 1.75 monolayers.

well separated in energy. This implies that the divalent and trivalent intensities can be monitored individually in great detail. Figure 4 shows the observed ratio between the Sm^{2+} and Sm^{3+} intensities as a function of coverage. At one monolayer the Sm film is completely trivalent. The second layer, however, becomes divalent. During the growth of this layer the divalent intensity increases rapidly. After completion of the second monolayer the divalent surface is fully developed and the next added Sm atom becomes trivalent; i.e., in this region the trivalent signal increases. In this way the completion of the second layer and thereby the first divalent surface layer is seen as a sharp maximum in the plotted $\text{Sm}^{2+}/\text{Sm}^{3+}$ intensity ratio. This maximum in Fig. 4 occurs at between 1.7 and 1.75 monolayers.¹² It can also be noted that the work-function versus Sm-deposition curve has a kink at the same coverage,¹¹ indicating that the third layer starts to grow.

In Fig. 4, one monolayer is defined as the coverage at which the *first* monolayer is completed. It has previously been found that an additional 5% are incorporated in the first layer during the growth of the second layer,¹⁴ obtaining the density of a close-packed Sm(0001) layer. In units of a fully contracted bulk Sm layer the kink therefore occurs at a coverage of between 1.62 and 1.67. This is in perfect agreement with the proposed structure in Fig. 2 and shows in an independent way that the surface layer is indeed expanded. The surface lattice parameter is 9% larger than expected for a close-packed divalent layer. It can be noted that the first hexagonal submonolayer structures of Sm and Yb adsorbed on Mo(110) also occur with 9% expanded lattice parameters,¹⁴ indicating dominating lateral interactions. In these cases it is energetically favorable to compress this hexagonal structure upon further deposition, while for the Sm surface it is more favorable to include additional atoms into the bulk.

The thermal behavior of the surface is also most interesting. At RT the 5×5 LEED pattern can no longer

be seen. We interpret this as a melting of the surface. The exceptionally low melting temperature can be understood in terms of both the site mismatch between the surface and bulk layers and the open nature of the surface layer. This possibility of a low surface melting temperature has been proposed as an explanation to the anomalously low melting temperature of Sm metal¹⁰ (100 K lower than expected). The disordering of the surface already at low temperatures also explains why previous attempts to observe the Sm reconstruction have failed.¹⁵ The disordering of the surface at room temperature is also consistent with the change of the photoemission spectra with temperature. In Fig. 3(b) is shown a spectrum recorded at 80 K of a sample which has been deposited at room temperature. When measured instead at RT, Fig. 3(a), the divalent surface features are much broader. This indicates either that there is a disordering of the surface or that there are large vibrational amplitudes for the divalent surface layer. Still in the spectrum measured at RT the surface features are sharper than those of normal evaporated Sm films indicating the more well-defined nature of the crystalline surface even when melted compared to polycrystalline surfaces. This is also illustrated by a spectrum, Fig. 3(c), of a thick film evaporated and measured at 80 K. The divalent surface features are very broad indicating that a distribution of surface sites with different coordination numbers exists.

To summarize, we have demonstrated that the Sm(0001) surface shows a 5×5 surface reconstruction. This is a new type of reconstruction which is caused by a valence transition of the surface atoms. The surface is divalent while the bulk is trivalent. The proposed surface reconstruction model corresponds to a 25% isostructural expansion of a trivalent bulk layer. The surface lattice parameter is 9% larger than that expected for a close-packed divalent layer. This, together with the mismatch between the first and second layers, leads to an exceptionally low surface melting temperature for Sm; already at room temperature the 5×5 LEED pattern has disappeared. The possibility that the low surface melting temperature for Sm may be related also to its anomalously low bulk melting temperature is pointed out. A possible reconstruction already at coverages around 2 ML is difficult to observe due to the multiple diffraction from the Mo substrate. The type of surface valence transition observed in Sm may occur in a few other cases. Americium may possibly show a similar reconstruction although it is still questionable if the surface really changes valence for a well-ordered surface of this element.¹⁶ Another most interesting candidate for a related effect, however, is α -cerium which can be predicted to have a larger degree of $4f$ localization for the surface atoms. Such a transition corresponds to the well-known α - γ transition for the bulk metal and would cause a similar size mismatch.

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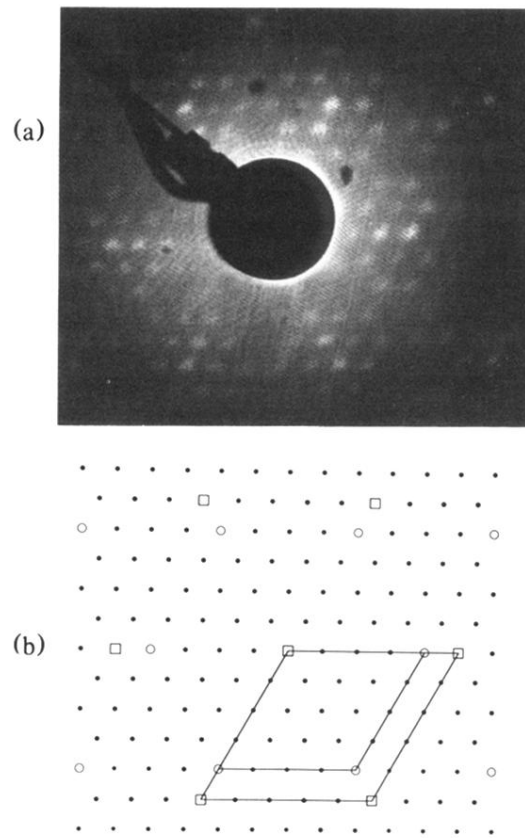


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