

Geometry of the Valence Transition Induced Surface Reconstruction of Sm(0001)

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We present a structural determination of the surface reconstruction of the Sm(0001) surface using surface x-ray diffraction, scanning tunneling microscopy, and *ab initio* calculations. The reconstruction is associated with a large (22%) expansion of the atomic radius for the top monolayer surface Sm atoms. The mechanism driving the surface reconstruction in Sm is unique among all elements and is connected to the strong correlations of the $4f$ electrons in Sm and the intermediate valence observed in certain Sm compounds. The atoms constituting the top monolayer of Sm(0001) have vastly different chemical properties compared to the layer underneath and behave as if they were an adsorbate of a different chemical species.

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The lanthanide metals and their compounds have been a challenge to solid-state physicists for many years because of their unusual electronic, magnetic, and structural properties. The strong correlations among the electrons of the partially filled $4f$ electron shell, and their interaction with the delocalized valence electrons are central to an understanding of these properties. The number of valence electrons may change from three to two by changing the surroundings of the atom such as the pressure, the temperature, or the coordination number of the lanthanide atoms. Such a valence transition influences many of the physical and chemical properties in a profound way. One example is SmS, which is a golden metal at room temperature (with trivalent Sm atoms) but bursts into black powder (having divalent Sm atoms) if cooled quickly. The existence [1–3] of a divalent Sm [$4f^6(6s6p5d)^2$] surface layer on a trivalent [$4f^5(6s6p5d)^3$] bulk for elemental Sm is an example of a valence transition induced solely by the lower coordination number at the surface. From theory [4,5], it has been estimated that the trivalent-divalent valence transition in Sm increases the radius of the Sm bulk atom by 12%.

This valence transition from trivalent in the bulk to divalent in the surface layer opens up the possibility to study a unique situation: despite the fact that the bulk and surface atoms in the two topmost layers in the film are of the same species, the size difference between them is significant. A structural study of such a fascinating system, on the atomic scale, is thus clearly motivated. In addition, the study also provides structural information, which may be used to test the application of current theory to $4f$ metals, and we make a comparison between experiments and state of the art first principles calculations.

The Sm(0001) surface was prepared by evaporating Sm onto a Mo(110) surface kept at room temperature. Despite the complicated stacking of Sm, evaporation of Sm

on Mo(110) at room temperature results in a layer-by-layer growth mode (see Fig. 2) of single crystalline Sm. The thickness of the Sm films was in all cases approximately 10 layers. The surface x-ray diffraction (SXRD) measurements were performed at the surface diffraction beam line [6] at the European Synchrotron Radiation Facility (ESRF). The wavelength of the incident x rays was set to 0.724 Å. The sample was aligned according to the bulk Bragg reflections of Sm. The geometrical structure was deduced by a best fit procedure between the experimental and calculated structure factors. Scanning tunneling microscopy (STM) measurements were performed in a UHV chamber with a base pressure below 8×10^{-11} mbar. All STM images were obtained in constant current mode with the sample bias negative. The cleanliness of the Mo(110) surface and of the Sm prepared surfaces were checked by Auger electron spectroscopy (AES); no or only very weak signals from contaminants such as carbon, oxygen, or sulfur could be detected. An impurity concentration of approximately 0.03 ML did not affect the surface properties. The first principles calculations were performed by the use of an all-electron, full potential linear muffin-tin orbital (FP-LMTO) method [7], and the valence stability of the surface was addressed using the method described in Ref. [8]. In this theory no approximation is made regarding the shape of the charge density or the effective potential. The calculations were made using the general gradient approximation to density functional theory [9].

Previously, a surface reconstruction of the Sm(0001) surface has been observed qualitatively [10] in low energy electron diffraction (LEED). In that study, the surface was observed to exhibit a 25% expansion of interatomic distances as compared to the bulk, leading to a (5×5) reconstruction. The complexity and the interpretation of a full surface structural determination of such a large surface

unit cell (25 atoms) is beyond the capability of present-day dynamical (multiple scattering) LEED theory. Instead, a natural choice for a structural study of the reconstruction is the technique of SXRD, since the scattering of x rays may be treated within a kinematical (single scattering) theory. In Fig. 1a, is shown a surface sensitive scan in reciprocal space from $H = 0.1$ to $H = 1.2$ with $K = 0$ and $L = 0.2$ corresponding to a scan along the $[100]$ direction of the hexagonal $\text{Sm}(0001)$ surface. As the scattered x-ray intensity from the bulk periodicity is found at $H = 1$, we expect to find the satellite spots due to the surface reconstruction at $H = 0.8$, corresponding to the previously observed (5×5) surface reconstruction. However, instead we find the surface diffracted x-ray intensity at $H = 0.82$. In addition, we observe faint satellite spots at $H = 0.18$ and $H = 1.18$ reciprocal lattice units as may be seen in Fig. 1b. Thus, the previous 5×5 surface reconstruction could not be confirmed, but instead we observe an incommensurate coincidence with the bulk periodicity.

In order to gain more information on this complicated surface reconstruction, we performed scanning tunneling microscopy (STM) measurements of the $\text{Sm}(0001)$ film. The general morphology of the surface of a ten-layer-thick Sm film deposited on the $\text{Mo}(110)$ substrate at room temperature is shown in the STM image in Fig. 2a. From this image, it is clear that the growth of the Sm film ap-

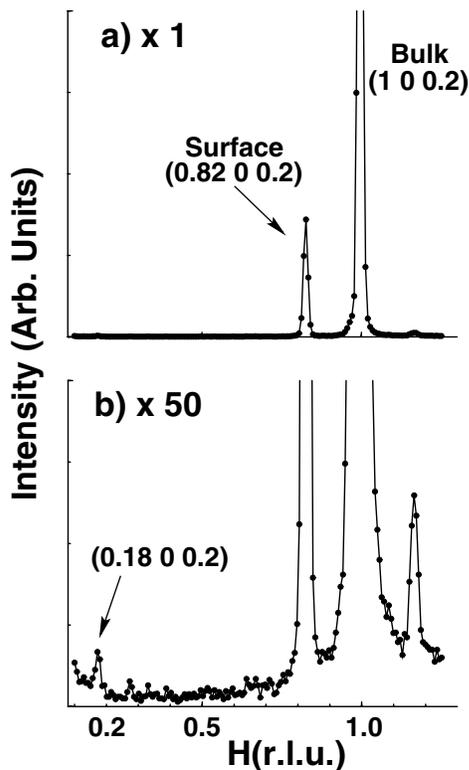


FIG. 1. (a) A surface sensitive x-ray scan along the (01) direction ($L = 0.2$). The diffraction due to the periodicity of the surface reconstruction can be found at $H = 0.82$. (b) The same as in (a) but expanded 50 times. Additional intensities observed at $H = 0.18$ and $H = 1.18$ can be seen, corresponding to a coincidence pattern (see Fig. 2).

pears to be flat, or two dimensional. Only three to four different terrace levels may be observed and the size of the terraces is on the average several tens of nanometers. By scanning the STM tip over a smaller area as shown in Fig. 2b, the periodicity of the surface corresponding to the surface reconstruction as observed by SXRD can be seen as darker periodic spots on the surface. The first direct observation of divalent Sm atoms is shown in Fig. 2c. In this figure, an STM image of a $10 \times 10 \text{ nm}^2$ area of the surface is shown, in which the divalent surface Sm atoms are resolved. It is immediately clear that the atoms form a hexagonal layer. However, it is also clear that some atoms or groups of atoms appear darker than the majority of the atoms, indicating a lattice distortion. The reason for this distortion is the trivalent Sm atoms in the layer directly underneath the surface layer. Since the trivalent Sm atoms are smaller than the divalent ones, the two lattices will have different lattice constants. As the two layers are incommensurate, the appearance in the STM image will be that of a moiré pattern. The darker atoms in the surface layer indicate coincidence sites producing the moiré pattern. By simply counting the number of atoms between the coincidence sites in the moiré pattern, we may determine the difference in lattice distance between the divalent and the trivalent lattices. As we find on average 4.5 divalent surface Sm atoms between the darker atoms, there must thus be on average 5.5 trivalent Sm atoms in the layer directly underneath the surface layer in order to produce the moiré pattern, indicating that the divalent Sm atoms have a 22% larger radius than the trivalent atoms, in perfect agreement with the above presented SXRD measurements.

By utilizing the direct information gained from the STM images with atomic resolution we may construct a model of the atomic arrangement of the $\text{Sm}(0001)$ surface reconstruction. In such a model, every ninth divalent Sm atom

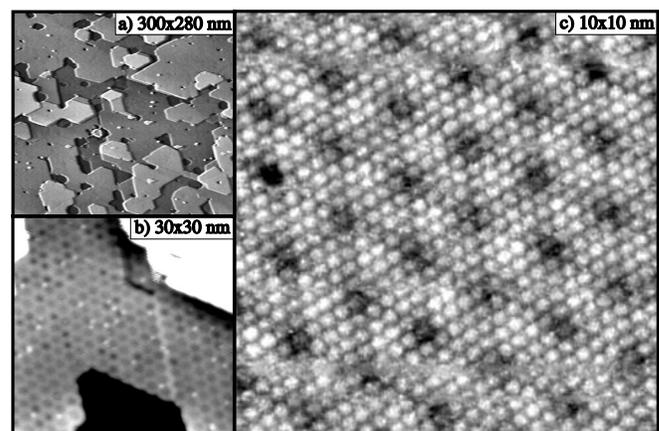


FIG. 2. STM images of (a) $280 \times 300 \text{ nm}^2$ large area of an approximately 10 layer thick Sm film. (b) $30 \times 30 \text{ nm}^2$ large area displaying the surface induced periodicity in the $\text{Sm}(0001)$ surface. (c) $10 \times 10 \text{ nm}^2$ large area displaying the divalent Sm atoms. The darker appearing atoms correspond to the coincidence between the divalent Sm surface atoms and the trivalent atoms in the layer underneath.

coincides with every eleventh trivalent Sm atom in the trivalent layer below, resulting, to a good approximation, in an 11×11 reconstruction. Using the nearest neighbor distance in bulk trivalent Sm, this results in a surface unit cell constant of 39.49 Å, corresponding to the distance between every second darker atom or groups of atoms observed in the STM image in Fig. 2c. Further, in the direction normal to the surface we use the c -bulk parameter of trivalent Sm equal to 26.207 Å. We use this model in order to fit a large number of collected SXRD structure factors, so that the details of the atomic arrangement of the surface reconstruction can be determined. The result of the best fit between the structure factors obtained from the experiment and the calculated ones [12] is shown in Fig. 3. The refined model after the fitting procedure is shown in Fig. 4. Because of the large number of atoms involved in the model, we have restricted ourselves to fit only the positions of the

atoms in the two topmost layers. The Sm atoms have been colored according to their atomic coordinates normal to the surface in order to display the oscillations and periodicity of the coincidence pattern (moiré pattern). Darker colors (brown-green) correspond to atoms deeper towards the bulk while lighter atoms (yellow-blue-white) correspond to atoms relaxing outwards. The best fit structure shows that the darker atoms in the STM image are due to divalent surface atoms which are situated directly in or close to on-top sites on the trivalent Sm atoms in the layer underneath. The fact that the on-top divalent Sm atoms relax towards the bulk is consistent with previous observations for other systems with the ad atoms being larger than the substrate atoms [13,14]. Such an inwards relaxation of the trivalent atom underneath the divalent atom in an on-top location reduces the bond length between the divalent and next nearest neighbor trivalent atoms thereby increasing the bond strength. The maximum amplitudes of the undulation of the divalent Sm surface layer are found to be close

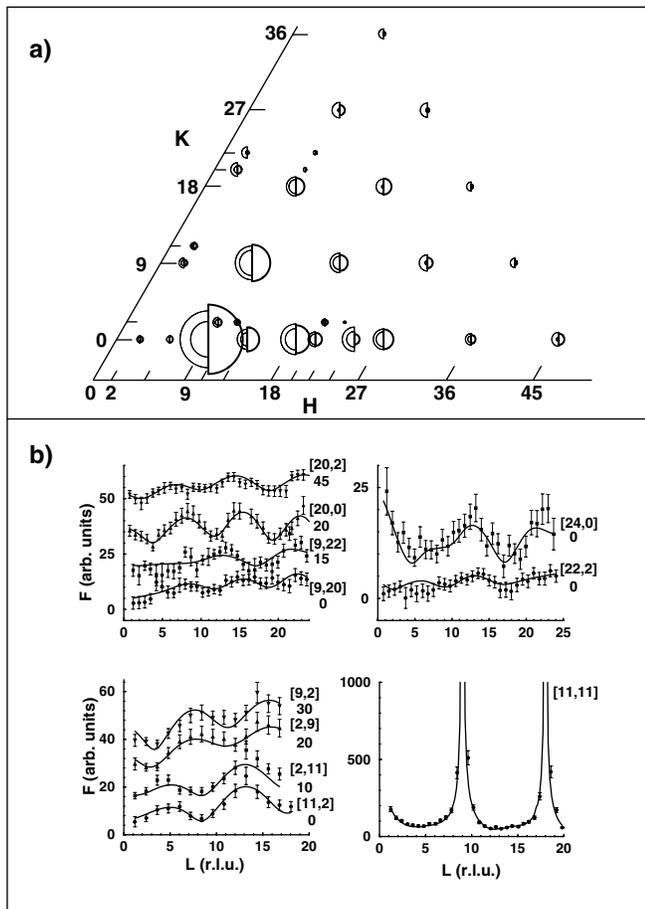


FIG. 3. (a) Experimental and calculated in-plane structure factors ($L = 0.2$) from the Sm(0001)-(11 × 11) reconstruction (see Fig. 4). The radius of the right half-open semicircles is proportional to the calculated structure factors. The double left open semicircles indicate the maximum and minimum experimental fractional and integer order structure factors. (b) Calculated and experimental order structure factors from the Sm(0001)-(11 × 11) reconstruction (see Fig. 4). For clarity, the number under the reflection label indicates the offset between this reflection and the first one.

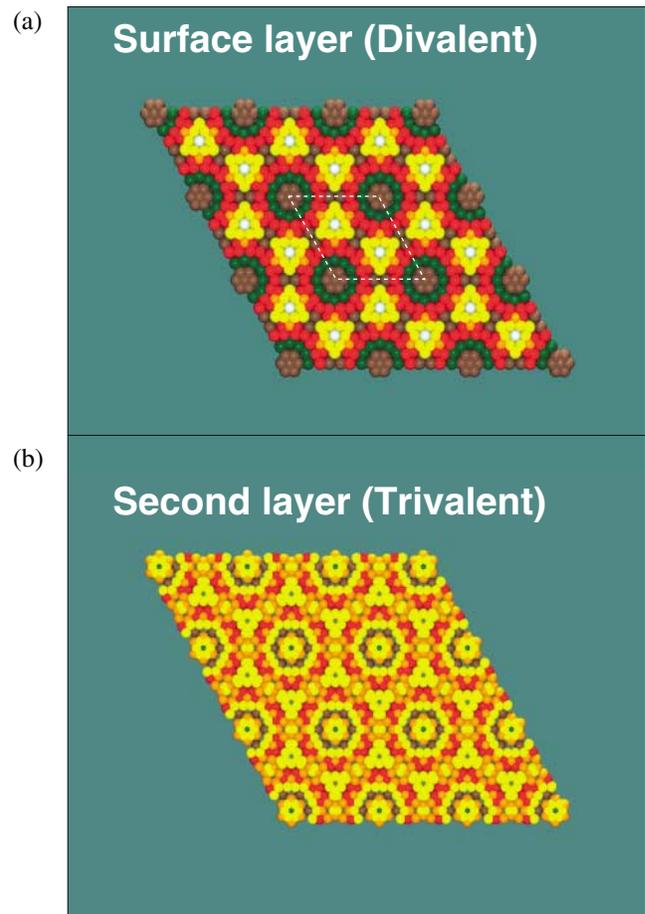


FIG. 4 (color). Model of the Sm(0001) surface consisting of the atomic arrangement of the two topmost layers at the surface. Darker atoms (brown) indicate a relaxation towards the bulk, while lighter atoms (white) indicate an expansion away from the bulk. (a) Top view of the divalent surface. The unit cell is indicated by the dashed line. (b) Top view of the trivalent second layer.

to 1 Å, while the maximum corrugation amplitude of the trivalent layer is found to be around 0.7 Å. The average interlayer distance, taking into account divalent Sm atoms in hollow, bridge, and on-top positions, between the divalent and trivalent layers is found to be 3.22 Å as compared to an ideal average interlayer distance of 3.55 Å. This 10% average relaxation reflects the local strong relaxation of the divalent Sm atoms in on-top or close to on-top locations. Finally, it should be noted that no rotation of the surface layer can be detected.

It is clear that the present results disagree with previous calculations [4,5] in which the radius of the Sm atom is predicted to expand a mere 12% in the transition from trivalence to divalence; that is, only about half of the radial expansion observed here. However, these calculations were performed for atoms situated in the bulk of a fictitious divalent Sm crystal. To shed light on this issue, we have performed first principles calculations of divalent and trivalent surfaces of Sm and we find that only the topmost surface layer of Sm is divalent; all other layers are trivalent. We also calculated the equilibrium lattice constant of the divalent surface layer (this time neglecting the effect of the lower atomic layers) and found a value of 4.24 Å (experiments yield 4.39 Å), which corresponds to a linear expansion of 17%. The improved agreement between the present calculations and experiments as compared to the previous bulk calculations, allows us to conclude that the effect of the surface induces an additional expansion of the divalent Sm atoms.

In conclusion, we report direct experimental observations of divalent Sm surface atoms. The divalent atoms form a complex arrangement, incommensurate with the Sm bulk. In fact, the Sm surface atoms behave chemically as if they were an adsorbate of a different chemical species, an observation consistent with the different chemical properties of divalent and trivalent lanthanide elements. This is further reflected in the fact that the surface reconstruction of Sm(0001) is the only metal surface reconstruction known produced by compressive stress. All other known reconstructions of metal surfaces, such as the surface type of Au(111) [15] are driven by an opposite tensile stress in the lattice of the surface layer. Our experimental results are compared to state-of-the-art, first-principles calculations. In agreement with our experimental observations, the divalent configuration of the Sm surface is found to be energetically more stable than the trivalent configura-

tion. The calculations also confirm that the surface itself induces an additional expansion of the divalent Sm atoms, not present in hypothetical divalent Sm bulk.

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