Magnetically ordered surface oxide on Gd(0001)

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Oxygen adsorption on Gd(0001) at 300 K leads to the formation of a well-ordered surface oxide with a characteristic occupied valence state, originating from hybridization between Gd 5d and O 2p states. This oxygen-induced state, which closely resembles the surface state of clean Gd(0001), has a binding energy of \( \approx 0.8 \) eV at \( \bar{\Gamma} \) and hence permits a detailed investigation by photoelectron spectroscopy. It exhibits a distinct temperature-dependent magnetic splitting, that remains finite above the Curie temperature.

In this paper, we report on such a well-ordered surface oxide on Gd(0001), which is magnetic and exhibits a characteristic occupied valence state with a binding energy (BE) of \( \approx 0.8 \) eV at the center of the surface Brillouin zone \( \bar{\Gamma} \). This valence state shows a magnetic splitting that decreases substantially with increasing temperature up to the \( T_C \) of bulk Gd (293 K), however, remaining at a constant value of \( (210 \pm 30) \) meV above \( T_C \). This behavior can be readily studied by PE only, in contrast to the partially occupied surface state of clean Gd(0001).

Angle-resolved PE spectra were recorded at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) at the TGM3, TGM5, and TGM6 beam lines, using a VSW ARIES hemispherical electron-energy analyzer with an angular resolution of 2°. The total-system energy resolution varied between 80 meV and 130 meV [full width at half maximum (FWHM)]. Resonant PE spectra were recorded at the SX700/II beamline, operated by the Freie Universität Berlin, using a Leybold EA-11 electron spectrometer. Gd(0001) surfaces were prepared by in situ film growth on a W(110) substrate, which could be cooled to \( \approx 50 \) K with a closed-cycle He refrigerator. 99.99% pure metal was evaporated from a Ta crucible heated by electron bombardment, with the substrate held at \( \approx 100 \) K. The film thickness was \( \approx 100 \) Å as determined by a quartz balance. The base pressure was \( 1 \times 10^{-11} \) mbar rising to \( 8 \times 10^{-11} \) mbar during evaporation. Under these conditions, contamination-free films could be grown as checked by surface-sensitive PE at 40-eV photon energy. Subsequently, these films were annealed to \( \approx 820 \) K, resulting in monocrystalline films, that exhibited very sharp hexagonal low-energy electron diffraction (LEED) patterns. Lu films of comparable quality, which

The local 4f moments of the lanthanides, which persist in the solid state, give rise to a number of unique magnetic phenomena and have attracted continued experimental and theoretical interest in these systems. 1 Especially Gd with its half-filled 4f shell and the highest magnetic ordering temperature among the lanthanide metals, has been studied intensively. 2–15 Controversial experimental results obtained from this local-moment system have led to a discussion of an enhanced Curie temperature \( (T_C) \) at the surface 2,9,16 and of the temperature dependence of the exchange splitting of valence states. 5,12–15 The discussion has focused on the surface magnetism was obtained. In a recent spin-polarized PE study of oxygen adsorption on Gd(0001), a suppression of surface magnetization was found that was explained by a reduced magnetic coupling strength caused by a loss of delocalized conduction electrons upon oxidation. 20 In this context, the discovery of an unusual metallic oxide on the surface of Lu(0001) is important. 21 In such a surface system, conduction electrons can be provided for an indirect coupling of 4f moments in analogy to the metallic bulk monosulfides. 22 Since Lu and Gd are very similar from a chemical point of view, an analogous oxide can be expected on Gd(0001).

Properties of surfaces can be studied by systematically modifying their electronic structure. Such experiments have been carried out on Gd(0001) by adsorption of hydrogen, 17 oxygen, 18 and nitrogen, 19 with the result that a clear suppression of surface-state emission was observed, but only very limited information about the influence of the adsorbants on the surface magnetism was obtained. In a recent spin-polarized PE study of oxygen adsorption on Gd(0001), a suppression of surface magnetization was found that was explained by a reduced magnetic coupling strength caused by a loss of delocalized conduction electrons upon oxidation. 20
have been studied as a nonmagnetic reference, were obtained by the same method. In the present experimental setup, film annealing led to minor oxygen contaminations, which could hardly be avoided, since a substantial amount of oxygen was frozen onto the cooled sample rod in the vicinity of the sample during preceding adsorption procedures. The resulting level of contamination of less than 0.02 ML, however, is not of any relevance for the present study. Well-ordered oxide phases with sharp 1 × 1 LEED patterns could be prepared on these Gd(0001) and Lu(0001) surfaces by exposure to ∼1 Langmuir (L) of oxygen and subsequent annealing. While for Lu, the annealing temperature was ∼700 K, only 345 K was applied in the case of Gd, because of oxygen desorption at higher temperatures. Gd₂O₃ films with thicknesses of ∼50 Å, which were studied for comparison, were also prepared in situ on W(110) by evaporation of sesquioxide powder from a Ta crucible heated by electron bombardment.

An overview of the electronic structures of various Gd surfaces is obtained from valence-band PE spectra recorded with 40-eV photon energy in normal-emission geometry at 50 K. Figure 1(a) displays the PE spectrum of a freshly prepared Gd(0001) surface, which is characterized by the pronounced emission from the surface state (S₁) at Eₚ = 6 eV and from the exchange-split Δ₂ bands (D) around 2-eV BE. The 4f states occur at ∼8-eV BE and the weak feature at ∼6-eV BE is due to the aforementioned minor oxygen contamination. Upon exposure to 1 L of oxygen and annealing, the spectral features change significantly. A very sharp O-2p-derived peak appears at ∼6-eV BE, while the surface-state emission is suppressed. Instead, two new features labeled S₂ appear at ∼0.8-eV BE. The corresponding spectrum from the oxide phase on Lu(0001) [Fig. 1(c)] reveals the same characteristics, however, with only a single feature S₂. As in the case of Lu(0001), the surface oxide on Gd(0001) does not represent the sesquioxide. This is evident from the corresponding spectrum of Gd₂O₃ displayed in Fig. 1(d), which reveals a broad O 2p emission and vanishing intensity at Eₚ according to its nonmetallic character. A hint at the character of feature S₂ can be obtained from the photon-energy dependence of the PE cross section. Figure 1 (inset) displays integrated peak intensities as a function of photon energy, normalized with respect to the incident photon flux. The behavior of S₂ is different from that of the surface state S₁, following the behavior of the O 2p emission with a broad maximum around 45 eV, indicating a close relationship between these states, presumably due to a significant mixing of O 2p and Gd 5d states at the surface.

Details of the change in the 4f-electronic structure of Gd(0001) upon oxidation can be inferred from the resonant PE spectra displayed in Fig. 2. These spectra were recorded at 148.5-eV photon energy corresponding to the maximum of the 4d→4f giant resonance. At resonance, the cross section of Gd 4f PE is strongly enhanced, allowing a detailed analysis of the 4f-spectral features with negligible influence of the otherwise interfering O 2p emission. Figure 2(a) displays the 4f emission from clean Gd(0001), which is characterized by two 7F final-state multiplets due to emission from bulk (b₁) and surface (s₁) atoms, separated by a surface core-level shift of (270±30) meV. Upon adsorption of 0.5 L of oxygen, the intensity of s₁ has decreased substantially, while two new components s₂ and b₂ appear, which are assigned to emission from the surface oxide and the subsurface layer, respectively. While component s₂ cannot be debated, b₂ is not readily distinguished in the spectra of Fig. 2. Such a component, however, has been clearly resolved in case of Lu (Ref. 21) and is necessary for a consistent description of the spectra 2(a)–2(c). Upon adsorption of ∼1 L of oxygen, the clean-surface component s₁ has almost vanished, being replaced by the oxygen-induced component s₂, which occurs at (640±50) meV higher BE as compared to b₁. The bulk component b₁ is unchanged and the subsurface component b₂ is shifted by (60±40) meV due to the presence of oxygen on the surface. The respective shifts in the case of Lu(0001) are significantly larger, ∼1.0 eV for s₁ and ∼230 meV for b₂, which corresponds very well to the stronger oxygen bonding on Lu(0001) than on Gd(0001) as indicated by the higher thermal stability, observed, e.g., during the annealing procedures. The behavior of oxygen on
Gd(0001) is in complete analogy to the case of Lu(0001), leading to the formation of a surface oxide, with negligible diffusion of oxygen into the bulk. This phase does not represent the sesquioxide, with the 4\textit{f}-electronic structure characterized by three broad features (inset of Fig. 2). It can rather be interpreted in terms of a monoxide phase with metallic character, resembling the electronic structure of the monosulfide\textsuperscript{21}

In view of the analogy to GdS, which exhibits antiferromagnetic order\textsuperscript{,25} interesting magnetic properties can be expected also for the present surface oxide, in particular, since the underlying bulk Gd film is ferromagnetically ordered. Its magnetic behavior can be readily studied by angle-resolved PE only, using the characteristic oxygen-induced feature \textit{S}\textsubscript{2}, which is essentially occupied and well separated from the Fermi energy, in contrast to \textit{S}\textsubscript{1}, which is only partially occupied.\textsuperscript{12–15} Unlike \textit{S}\textsubscript{1}, \textit{S}\textsubscript{2} is located close to the lower edge of the band gap around the center of the Brillouin zone. It exhibits properties of a surface state, with no dispersion along Γ\textit{A} perpendicular to the surface. Similar to \textit{S}\textsubscript{1}, it disperses along Γ\textit{K}, however, towards lower BE, while \textit{S}\textsubscript{1} disperses towards higher BE (spectra not shown here). This characteristic of \textit{S}\textsubscript{2}, on the other hand, is not surprising, since it reflects the behavior of the bulk bands close to the lower gap edge.\textsuperscript{3} Thus, the oxygen-induced state \textit{S}\textsubscript{2} closely resembles the surface state of clean Gd(0001), being localized in the topmost layer, however, with a higher BE due to the interaction with O 2\textit{p} states. As inferred already from Fig. 1(b), feature \textit{S}\textsubscript{2} reveals a distinct splitting at low temperatures that is not observed in the case of Lu with a closed 4\textit{f} shell, and therefore is necessarily related to the 4\textit{f} moment of Gd.

Details of \textit{S}\textsubscript{2} are shown in Fig. 3, which displays angle-resolved PE spectra recorded in normal emission at various temperatures below and above the \textit{T}_\textsubscript{C} of bulk Gd metal. Besides the oxygen-induced feature \textit{S}\textsubscript{2} at \textapprox\,0.8-eV BE, also emission from the bands of the underlying bulk Gd (\textit{D}) can be observed around 1.8 eV. Both features are split into two components, which are easily resolved at 52 K. The splittings of \textit{D} and \textit{S}\textsubscript{2} decrease with increasing temperature, with no changes observed above \textit{T}_\textsubscript{C} in both cases. While the bulk-band splitting collapses to zero, a finite splitting persists for \textit{S}\textsubscript{2}, as can be inferred from the strongly asymmetric shape of this feature even at 345 K. Such an asymmetry is not observed in the PE spectrum from the respective oxide on Lu(0001), recorded at 50 K (top of Fig. 3), providing further evidence for a magnetic origin of the splitting in case of Gd.

For a quantitative description of the temperature dependence of the splitting, a least-squares-fit analysis was applied, as represented by the solid lines through the data points. The spectra are readily described by pairs of symmetric Lorentzians for the emissions \textit{D} and \textit{S}\textsubscript{2} (solid subspectra), respectively, and a smooth background (dotted lines). Note that for Lu, \textit{S}\textsubscript{2} is described by a single symmetric Lorentzian. The results of the fit analysis are summarized in Fig. 4, which displays (a) the BE’s and (b) the splittings of \textit{D} and \textit{S}\textsubscript{2} as a function of temperature. The bulk-band states (squares) show a decreasing splitting as found in other studies,\textsuperscript{5,12} eventually collapsing to zero at \textit{T}_\textsubscript{C}\,=\,293 K within the experimental uncertainty of \textapprox\,100 meV. A decrease of the splitting is also found for the oxygen-induced feature \textit{S}\textsubscript{2}, from (460±20) meV at 52 K to (210±30) meV at \textit{T}_\textsubscript{C}. In constrast to the bulk-band behavior, a temperature-independent finite splitting is observed above \textit{T}_\textsubscript{C}, as in tunneling spectra from the surface state of clean Gd(0001).\textsuperscript{15} Since the latter observation is at variance with results from PE and IPE,\textsuperscript{13,14} it is not clear at present, if the magnetic behavior of \textit{S}\textsubscript{1} and \textit{S}\textsubscript{2} is identical.

In conclusion, an epitaxial surface oxide has been prepared on Gd(0001), which is distinctly different from the sesquioxide and rather has to be identified with a monoxide as in case of Lu(0001). In this surface oxide, no suppression of magnetization was found, in contrast to the conclusions of
Ref. 20. It reveals a characteristic valence state at \( \approx 0.8 \text{-eV} \) binding energy, that can be used to study its magnetic properties. This oxygen-induced state closely resembles the surface state observed for clean Gd(0001), but can be readily studied by photoemission only, in contrast to the latter. This state exhibits a temperature-dependent magnetic splitting, providing evidence for magnetic order in the surface oxide up to the Curie temperature of bulk Gd. Above \( T_C \), a persisting temperature-independent splitting is observed, which is direct evidence for such a phenomenon in a local-moment system from photoemission, for which \( k \) selectivity ensures a straightforward identification of spectral features. Interesting open questions concern the magnetic structure and the role of the underlying ferromagnetically ordered bulk Gd. Similar oxide phases can be expected for the close-packed surfaces of other heavy lanthanide metals, offering new perspectives for the study of surface magnetism in these systems.

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