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Oxygen Induced Suppression of the Surface Magnetization of Gd(0001)

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The effects of oxygen adsorption on the surface magnetization of Gd(0001) have been determined by measuring the polarization of the Gd 4*f* core levels and the oxygen induced states with spin-resolved photoemission. Calculations of the partial density of states of O/Gd(0001) using the LMTO-ASA method support the photoemission measurements, which indicate that oxidation occurs at low coverages. The loss of surface magnetic order with oxygen exposure is explained in terms of decreasing indirect coupling.

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Almost all practical magnetic materials require a rare earth because of its large moment and anisotropy. Unfortunately, rare earths oxidize easily, thereby losing their useful magnetic properties. Therefore it is important to carry out studies that shed light on the physical mechanisms responsible for the changes in the magnetic properties of a rare earth with oxidation. The interatomic interactions among the highly localized 4*f* moments in a rare earth solid are mediated through *s-p-d* conduction electrons [1–4]. To study the changes in the electronic structure responsible for the magnetic properties of a rare earth upon oxygen adsorption, we have performed spin-resolved photoemission measurements of Gd 4*f* core levels and the oxygen-induced states. In addition, we have carried out self-consistent spin-polarized calculations to complement the experimental data.

The experiments were performed in a UHV chamber equipped with a spin-resolved electron analyzer described in detail elsewhere [5]. Well ordered crystalline Gd(0001) films, nominally 80 Å thick, were prepared *in situ* via thermal desorption onto a W(110) single crystal at room temperature [1,2,6,7], and subsequently annealed to 780 K to obtain well ordered films. The specific details of the experiment are presented in greater detail elsewhere [2,6]. The Gd(0001) films were magnetized in plane with a pulsed field, and all spin-resolved spectra were acquired in remanence. All of the photoemission spectra were acquired with a photon energy of 70 eV and at a sample temperature of 130 K.

The Gd 4*f* core levels can be deconvoluted into surface and bulk components as a consequence of the surface-to-bulk core level shifts [4,8–10]. Using spin-resolved photoemission, we have been able to determine the surface-to-bulk component shift of the Gd 4*f* core levels, as well as changes in the binding energies of the surface and bulk components as a function of oxygen dosing. In Fig. 1 we present the spin-integrated spectrum of the 4*f* core level of

clean Gd(0001), as well as the spin majority and minority components. We have neglected multiplet splitting as it only introduces ambiguity, and such fits are highly suspect. We have used a Doniach-Sunjić line shape [11] to fit the clean Gd 4*f* core level, as well as the spectra following oxygen adsorption. We have determined the surface-to-bulk 4*f* core level shift to be 400 ± 20 meV. This shift is obtained for both the spin-integrated spectrum and the spectra of both the majority and minority spin components. These results are generally consistent with the majority of the previous measurements of the (0001) surface of Gd [4,8,10]. In addition, the deconvolutions of the majority and minority components indicate that the surface is ferromagnetically coupled to the bulk, in agreement with earlier studies [10,12].

With increasing oxygen dosing the surface-to-bulk core level shift is reduced from approximately 400 to 250 meV. The reduction of the Gd surface-to-bulk shift at an O exposure of 0.25 L (1 L = 10^{-6} Torr s) is due to a smaller shift to higher binding energies of the surface component (from 8.75 to 8.85 eV), as compared to the bulk component (8.35 to 8.60 eV). The larger shift of the bulk component is consistent with initial bonding in subsurface sites, as determined by an earlier spin-integrated photoemission study of oxygen adsorption on Gd(0001) [6]. We therefore conclude that oxygen goes to subsurface sites at initial stages of adsorption.

We can understand the physical origin of the larger binding energy shift of the bulk component of the Gd 4*f* core levels with oxygen adsorption by examining the differences between the local electronic environments of the surface and subsurface before and after oxygen adsorption (see Fig. 2). The higher binding energy of the surface component of the Gd 4*f* core levels for clean Gd(0001) is a consequence of the reduced coordination at the surface, relative to the bulk, which in turn reduces the screening of the gadolinium atoms at the surface [13]. In

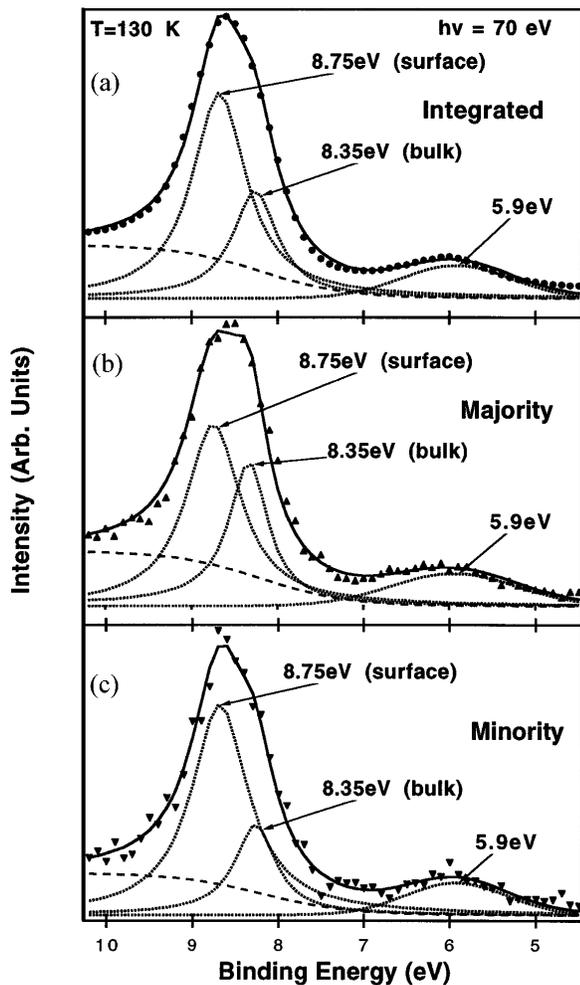


FIG. 1. Photoemission spectra of the $4f$ core levels of clean Gd(0001), (a) spin integrated, (b) the spin-majority component of the spin-integrated spectrum in panel (a) and (c) the spin-minority component of the spin-integrated spectrum in panel (a). The symbols are the data, and the solid lines are the fits of the data using a Doniach-Sinjac line shape. The dashed lines represent the deconvoluted surface and bulk components of the respective spectra. Panels (b) and (c) are expanded relative to (a) in order to show the details of the fits.

contrast, the subsurface maintains the bulk coordination and has greater Gd $5d$ itinerancy and hence more efficient screening [1]. The greater localization of $5d$ surface states of Gd(0001) supports this view [1]. The hybridization of the oxygen $2p$ orbitals with the $5d$ surface state of Gd will not reduce the screening parameter of the $4f$ core levels at the surface as significantly as hybridization with the bulk d bands upon subsurface absorption. This is supported by the large shift of the bulk component to a binding energy of 8.60 eV with an oxygen exposure of 0.25 L, as determined from the deconvolution of the spin-integrated and spin-resolved spectra.

Self-consistent spin-polarized electronic structure calculations have been carried out using the linear-muffin-tin-orbital method in the atomic sphere approximation for

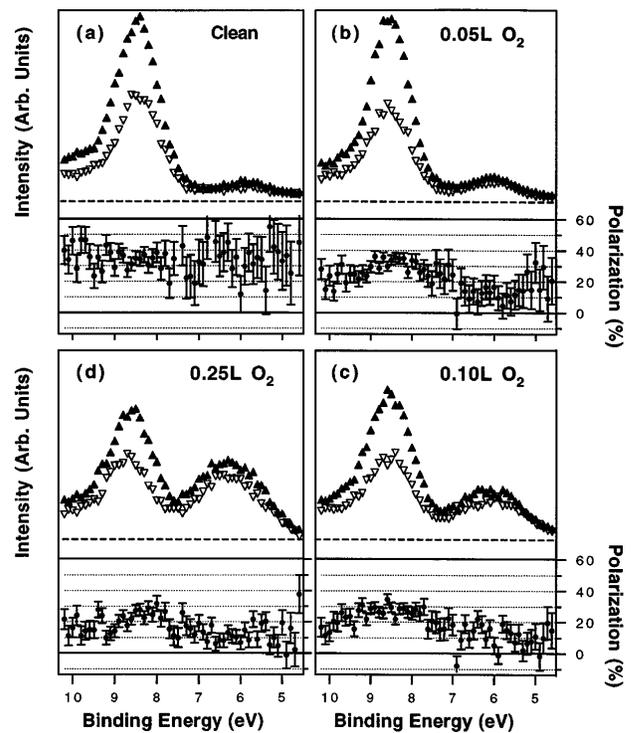


FIG. 2. The normalized spin-polarized photoemission spectra of the Gd $4f$ core levels as a function of oxygen exposure: (a) clean, (b) 0.05 L, (c) 0.10 L, and (d) 0.25 L. The closed triangles are the majority components, and the open triangles are the minority components. The polarization is displayed below each spectra.

O/Gd(0001). The Gd surface is simulated by constructing a three-dimensional crystal made up of an eleven-layer (0001) Gd slab and a three layer empty-sphere slab, with the bilayer slab repeated periodically. Additional empty spheres are also inserted at the interstitial sites halfway between adjacent layers and equidistant from the six nearest-neighbor sites in those layers. The two positions considered for the O layer are the interstitial empty spheres just above and below the three-fold hollow sites of the Gd surface layer. This gives a fairly complex hexagonal structure with 24 sites per unit cell (11 Gd, 11 empty spheres, and 2 O). The nearest-neighbor Gd-O distance for O on top has been set to be the same as that in the GdO₂ crystal (2.32 Å). The Gd $4f$ states, being fairly localized, are treated as fully polarized core states. The calculations have been carried out for 37 k points in the irreducible part of the Brillouin zone, which is reasonable for the large unit cell of this system. Based on the experimental evidence, these calculations assume ferromagnetic coupling between the layers.

The partial density of states (PDOS) of the two calculations for oxygen adsorption above the surface and below the surface Gd layer are presented in Fig. 3. For both sets of calculations, we have displayed the PDOS of oxygen, the surface layer of the Gd slab, and the second Gd

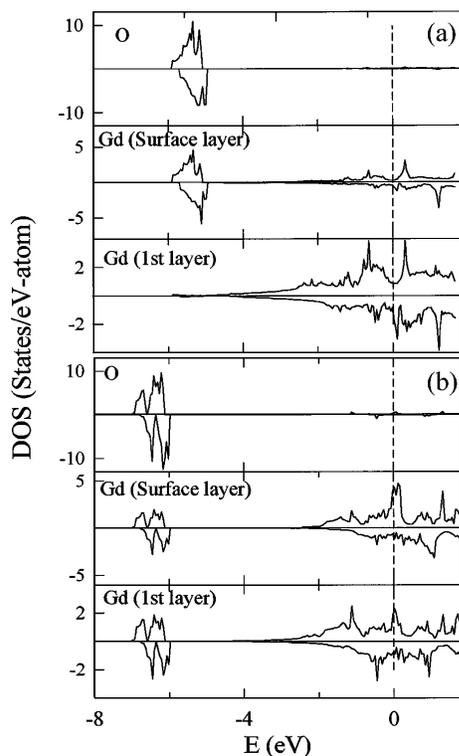


FIG. 3. The calculated partial density of states, reference to the Fermi level, of oxygen (top panel), the gadolinium surface (middle panel), and the first subsurface gadolinium layer (bottom panel) for (a) oxygen sites above the three fold hollow of the Gd surface and (b) for oxygen sites in the threefold hollow between the Gd surface layer and the next layer below.

layer. The PDOS for other Gd layers in both the calculations are similar to that of the second layer in Fig. 3(a) and show no hybridization with O. The O-induced bands lie in the region of 5–7 eV for the top and underlayers, respectively, and are in very good agreement with this study and earlier photoemission results [6]. Oxygen hybridizes very strongly, but only with nearest-neighbor Gd atoms. This results in a large number of the Gd s,p,d states near the Fermi level to be pulled down to the location of the O bands. Therefore the strong 6 eV oxygen-induced feature in the Gd PDOS (Fig. 3) implies early oxide formation at low oxygen exposures (0.25 L), i.e., the 6 eV oxygen-induced feature is not due solely to the introduction of a density of states from the oxygen, but also contains a contribution from the Gd states pulled down from near the Fermi level, indicative of oxidation.

We have observed noticeable changes in the structure of the polarization of the Gd 4*f* core levels, as well as in the vicinity of the oxygen-induced states (6 eV binding energy). In Fig. 2(a) the polarization of the Gd 4*f* core level for clean Gd is displayed below the set of spin-resolved spectra. Note that the polarization is relatively flat across the 4*f* core level region (7.5–9.5 eV binding energy). While there is scatter in the polarization in the

region where oxygen-induced states would form (5–7 eV binding energy), the average polarization is essentially equivalent to the 4*f* region. This indicates that the background is equivalently polarized with the Gd 4*f* core levels at an average value of 33%, in agreement with secondary electron polarization measurements [2]. For small quantities of oxygen exposure, a dip is observed in the polarization centered at about 6 eV binding energy [see 0.05 L exposure in Fig. 2(b)] and should be taken as a signature for the presence of oxygen.

Examination of the polarization spectra demonstrates that oxygen adsorption suppresses the magnetic order of the surface, as well as in the subsurface. This is an anticipated consequence of modifying the magnetic coupling between the Gd 4*f* core levels and the conduction electrons due to hybridization of the Gd $s-p-d$ bands with the O p bands. From Fig. 2(c) we see that at an oxygen exposure of 0.10 L the polarization begins to decrease in the regions of the 4*f* core levels and the O-induced states. The polarization of the background should be equivalent both at binding energies less than the O-induced states and at binding energies greater than the Gd 4*f* levels. As can be seen from Fig. 2, the averages of these two regions are indeed equivalent. Examination of Figs. 2(a) and 2(c) reveal that the polarization of the background also decreases at an oxygen exposure of 0.10 L. At an exposure of 0.25 L of oxygen, the peak in the polarization spectrum in Fig. 2(d) is much narrower than at lower exposures, even though the Gd 4*f* core levels still exhibit a polarization of approximately 30%. This is a consequence of the reduction in the polarization of the surface component of the Gd 4*f* core level, as well as a reduction of the Gd 4*f* surface-to-bulk core level shift, as discussed above.

The polarization spectra in Fig. 2 reveal that early stages of oxygen adsorption decrease the overall polarization of the surface. In addition, the diminishing structure of the polarization curve at an exposure of 0.25 L of oxygen is a consequence of the reduced magnetic order of the surface and the subsurface planes, and demonstrates that subsurface oxidation occurs at very low exposures (0.25 L or less). Wandelt and Brundle [14] indicated from ultraviolet and x-ray photoemission spectroscopy studies of oxygen adsorption on Gd that oxide formation occurs at an oxygen exposure of 0.8 L. Our results demonstrate that oxidation occurs at much lower exposures, with an upper limit of 0.25 L of oxygen.

Analysis indicates that the decrease in the polarization at a binding energy of 6 eV is not due to antiferromagnetic coupling of the oxygen-induced states, but is due to the nonmagnetic character of the oxygen-induced states. This is supported by the LMTO-ASA calculations for adsorption of O at surface and subsurface sites. In both cases, the oxygen-induced states have a negligible induced moment. The magnetic moments of the Gd sites are relatively unchanged with oxygen adsorption (<0.5%).

Oxygen adsorption has the effect of pulling the Gd s , p , and d bands down from the Fermi level through hybridization with the O p bands. This in turn reduces the indirect coupling of the s - p - d bands with the Gd $4f$ core levels, which is crucial to the long range magnetic order of the system. This is consistent with earlier measurements indicating pronounced final state effects resulting from reduced itinerancy following exposure to oxygen [8].

The effects of oxygen adsorption on the magnetic properties of Gd are in stark contrast to the oxidation of other magnetic materials, in particular, O/Fe(001) [15]. As with O/Gd(0001), the initial oxygen adsorption sites for O/Fe(001) are subsurface. Unlike O/Gd(0001), there are significant changes in the spin polarization of the shallow core levels ($3p$) of Fe with oxygen exposure. Spin-resolved photoemission of the Fe $3p$ core levels revealed a chemical shift corresponding to the presence of Fe³⁺ ions, and that this iron phase correlated with flips in the majority- and minority-spin populations, as compared to pristine Fe. It was concluded that at initial oxygen exposure a ferromagnetic γ -Fe₂O₃ phase develops as a consequence of antiferromagnetic coupling between the top layer of Fe and the underlying Fe layer by superexchange through the oxygen atoms embedded between the two Fe layers.

In conclusion, we have measured the magnetic order of the (0001) surface of gadolinium as a function of oxygen adsorption by measuring the polarization of the Gd $4f$ core levels and the oxygen-induced states using spin-resolved photoemission. The effects of oxygen adsorption is an overall reduction of the polarization of the electron background and the Gd surface state. The decrease in the polarization is accompanied by an increase in the binding energies of the surface and the bulk components of the $4f$ core levels as a consequence of final state effects. Our results suggest that gadolinium oxide forms with oxygen exposures as low as 0.25 L. The loss of magnetic order is explained in terms of a reduction in the exchange coupling between the $4f$ core levels through the conduction electrons as a consequence of hybridization of the Gd s - p - d bands with the oxygen p bands. The oxygen sites negligible moments in the ground state calculation, which

are supported by the spin-resolved photoemission, are not antiferromagnetically coupled to Gd nearest neighbors.

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