Surface Magnetism of Gd(0001): Evidence of Ferromagnetic Coupling to Bulk

G. A. Mulhollan, K. Garrison, and J. L. Erskine
Department of Physics, University of Texas, Austin, Texas 78712
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Previous polarized electron experiments and recent *ab initio* calculations suggest that the surface layer magnetic moments of Gd(0001) are antiferromagnetically coupled to the bulk magnetic moments. Spin-polarized photoemission data are presented which show that the spin polarization of the magnetic surface state and the surface $4f$ states of Gd(0001) are coupled ferromagnetically to the bulk magnetic moment.

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Gadolinium has been considered an important prototype material for testing local-spin-density approximation (LSDA) calculations on rare-earth metals where localized $4f$ electrons, exchange, and relativistic (spin-orbit) effects play important roles [1–6]. In the rare earths, the LSDA appears to overestimate the itineracy of $4f$ levels leading to predictions of structural, electronic, and magnetic properties often in relatively poor agreement with experiment, a few exceptions being La and Lu which have either an empty or filled $4f$ shell. Calculations for bulk Gd typically yield lattice constants which vary by a factor of 2 beyond limits considered appropriate for systems where the LSDA is judged accurate. LSDA calculations of band structure and magnetic properties are often in reasonable agreement with experiment. Recent self-consistent calculations for bulk Gd have yielded a conduction-band magnetic moment per atom ($\sim 0.57\mu_B$) in good agreement with measurements (~ 0.63), and an average $5d$-band exchange splitting (~ 0.6 eV) in reasonable agreement with recent angle-resolved photoemission measurements [7] of the Δ_2 band dispersion and exchange splitting. However, the binding energies and dispersion of the Δ_2 bands obtained from existing LSDA calculations do not agree with experimental results ($\sim 50\%$ discrepancies), suggesting either inaccuracies in the calculations, influence of surface effects due to short electron mean free paths [8], or strong many-body effects [9] in the photoemission similar to those apparent in Ni.

Surface properties of Gd(0001) are of intrinsic interest and also provide an additional means of testing LSDA calculations. Previous surface-sensitive probes of magnetism applied to Gd(0001) have established novel behavior. Spin-polarized low-energy electron-diffraction (SPLEED) and magneto-optic Kerr effect (MOKE) measurements [10] of single-crystal Gd(0001) surfaces [11] prepared on W(110) confirmed the existence of enhanced surface ferromagnetic order at temperatures up to 310 K (~ 20 K above the bulk Curie temperature $T_{Cb} = 293$ K). These results, along with spin-polarized photoemission experiments [10] that probed bulk and surface $4f$ excitations, were interpreted as indicating antiferromagnetic coupling between the surface $4f$ spins and those of the underlying ferromagnetic bulk.

Recent *ab initio* calculations [12] have examined the structural, electronic, and magnetic properties of Gd(0001), taking into account the total system energy. Several important results were obtained that can be directly compared with experimental results: First, the surface Gd atoms were found to occupy hcp sites on the lattice, and the outermost interlayer spacing was found to be expanded by $\sim 6\%$ compared with the bulk interlayer spacing; second, the surface Gd layer was found to couple antiferromagnetically with the underlying bulk ferromagnetic layers; and third, a localized d_{z^2} surface state was found to exist near $\bar{\Gamma}$ of the two-dimensional Brillouin zone. In the antiferromagnetically coupled Gd(0001) surface layer, the minority spin surface state band is occupied and the majority spin band is empty; the opposite is true for the ferromagnetically coupled layer. These calculations also presented angular momentum decomposed spin-polarized density of states and two-dimensional bands which are useful for analyzing photoemission results.

Existing experimental results [13,14] appear to support some of these predictions. Recent low-energy electron-diffraction studies of Gd(0001) are consistent with an hcp surface atom location, but also suggest that the surface layer is contracted about 3% rather than expanded 6%. Angle-resolved photoemission studies of both bulk Gd(0001) [7] and (relatively thick) Gd(0001) single-crystal films [15] grown on W(110) have confirmed the existence of a surface state near E_F and centered around $\bar{\Gamma}$ of the two-dimensional Brillouin zone. This result is consistent with the calculations, but the experiments were not able to determine the spin polarization of this state or even confirm if it is magnetic. While the previous spin-polarized photoemission experiments [10] of Gd(0001) did manifest evidence of antiferromagnetic alignment between surface and bulk $4f$ electron spins, the statistics and quality of experimental data were not convincing. In addition, no evidence of the surface state or of exchange split Δ_2 symmetry d states were reported in conjunction with the $4f$ level spectra—such information would have been useful in judging the surface conditions present during the experiment. More recent measurements of the $4f$ core-level polarization have failed to unambiguously pin

down the nature of the coupling [16].

In this Letter, we present spin- and angle-resolved photoemission data for Gd(0001) crystals grown on a W(110) surface. Our new data include polarization determination of electrons emitted from the surface state, the exchange split Δ_2 symmetry bulk *d* bands, and the 4*f* levels of both surface and bulk atoms. The results are consistent with *ferromagnetic* coupling between bulk and surface layers. Additionally, our spin-integrated spectra agree very well with our previous work on both bulk [7] and thin-film [15] Gd(0001) samples obtained using a different beam line.

Our experiments were conducted at the National Synchrotron Light Source using the U5 spin-polarized beam line. Undulator radiation was dispersed by a 6-m toroidal grating monochromator, and polarized photoemitted electrons were analyzed by a commercial 50-mm hemispherical analyzer fitted with a low-energy spin-polarization detector [17]. Thick Gd(0001) films were grown on W(110) substrates held at 450°C while evaporating Gd at a rate of 0.5 Å/s (same parameters as Ref. [10]) from an electron-beam-heated crucible [18]. Polarized electron measurements were taken on in-plane remnantly magnetized single-domain samples [11] with photons incident at 35° with respect to the surface normal. The magnetization was periodically reversed by application of current pulses through a coil located near the sample having an axis perpendicular to the polarization of light. The substrates and Gd(0001) crystals were examined by LEED to confirm the crystal integrity.

Figure 1 displays a comparison of (non-spin-resolved) angle-resolved photoemission spectra obtained at beam line U16A using a bulk Gd(0001) single crystal [7] and an epitaxial Gd(0001) film (~90 Å thick) obtained at beam line U5. The overall energy resolution at U16A was ~100 meV for the bulk sample; the corresponding resolution at U5 was ~300 meV. This difference in resolution accounts for the small but apparent difference in the surface state peak binding energy and its amplitude. Otherwise, the spectra are in excellent agreement. Figure 2 displays spin-resolved spectra showing a very strong positive spin polarization of the surface state peak, and an exchange splitting of the Δ_2 band consistent with reported results based on nonpolarized photoemission [7]. The upper peak of the exchange split pair clearly corresponds to the minority spin band. The locations of the Δ_2 bands as determined from the spin-resolved intensities are shifted slightly to lower binding energies from the previously reported values; the change is a result of the additional spectral resolution that polarization measurements yield. Broad scans that include emission from 4*f* levels as well as the surface state and Δ_2 bands clearly show that the 4*f* spin polarization is the same as that of the surface state and the majority spin Δ_2 subband. This suggests that spins in the surface and bulk layers are ferromagnetically aligned.

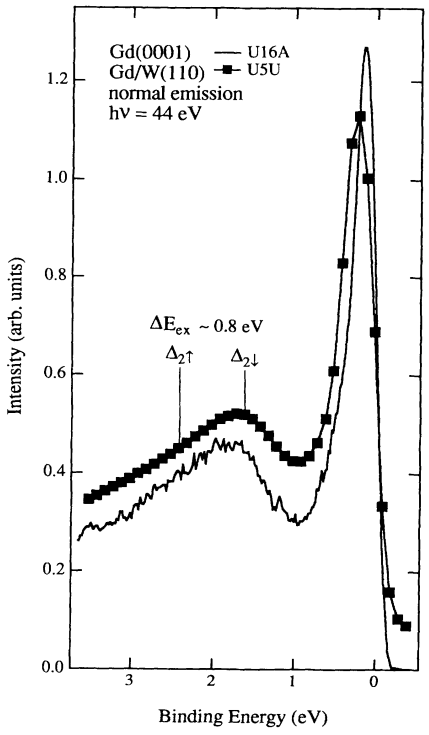

FIG. 1. Angle-resolved valence-band photoemission spectra from the surfaces of Gd(0001) and Gd/W(110) acquired at the U16A and U5U beam lines, respectively. The locations of the exchange split Δ_2 bands as obtained from Fig. 2 are noted.

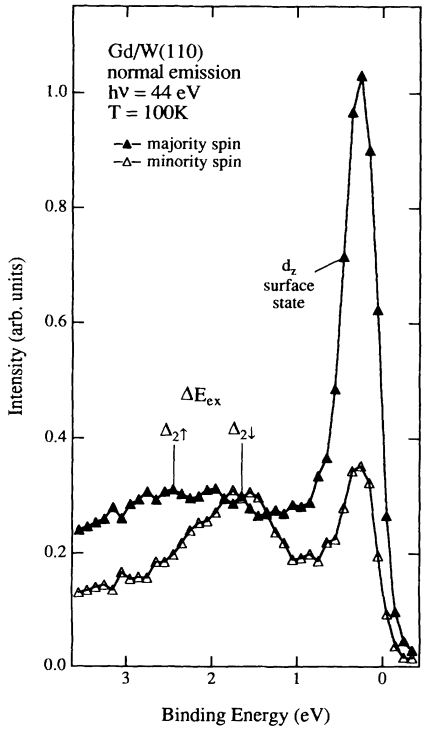

FIG. 2. Spin-resolved intensities obtained from the U5U data of Fig. 1.

Figure 3 verifies the ferromagnetic alignment between surface and bulk atom $4f$ spins by examining the polarization from surface and bulk $4f$ levels. The statistical spread of data shown in Fig. 3 is much smaller than in the previous experiments, and the data permit meaningful curve-fitting procedures to be employed that take into account both well-known methods of extracting rare-earth surface and bulk $4f$ binding energies and our instrumental broadening. The surface-shifted and bulk peaks were each modeled by seven Doniach-Sunjic lines in order to account for the final-state multiplet splitting of the $4f$ levels. The relative spacings of the lines within each multiplet [19] were fixed while a scaling factor permitted the absolute values to vary. The relative amplitudes of the multiplet lines were set using the fractional parentage calculations of Cox [20]. The Doniach-Sunjic line-shape parameters, surface core-level shift, and the relative surface to bulk line intensities were also permitted to freely vary. The results of the nonlinear least-squares curve fitting are shown in Fig. 3. The surface peak is shifted by 0.45 ± 0.04 eV to a higher binding energy than the bulk line. The surface shift and relative contributions from the bulk and surface-shifted $4f$ core-level intensities (ratio of 0.8) to the polarization are comparable and consistent with the trend in photon energy reported by Kammerer *et al.* [21]. The polarization due solely to the $4f$ manifold was calculated at each energy from fits to the spin-resolved intensities. The result, which is simply the polarization data with the background contribution removed, is shown in Fig. 3 as a shaded bar. The $4f$-derived polarization is manifestly positive for all energies with an amplitude of $\sim 52\%$. If the surface were antiferromagnetically coupled to the bulk, the $4f$ polarization would change from positive to negative upon going from low to high binding energy. The constant value of the $4f$ polarization confirms the nature of the coupling as deduced from the polarization of the surface state.

The magnitude of the $4f$ polarization, however, is smaller than initially expected. A naive interpretation of the photoemission process suggests that the polarization of the $4f$ photocurrent should be $\sim 80\%$ at 100 K. Depolarization measurements of the photocurrent emitted from Gd-coated Ge have revealed a short spin-dependent mean free path consistent with strong spin-exchange scattering in Gd [22]. A reduction in polarization is also consistent with the adsorption of large quantities [> 0.5 L (where 1 L $= 10^{-6}$ Torr s)] of hydrogen [23]. This possibility can be discounted in our case as the polarization showed little diminution after 4 h exposure to the background gases present at 1.5×10^{-10} Torr. Our measured value of 52% is most probably a manifestation of the strong spin-flip character of electron scattering in Gd.

In conclusion, we have shown new data that clearly establish the existence of ferromagnetic alignment between the bulk and surface $4f$ levels in Gd(0001) and the ferromagnetic nature of the d_{z^2} surface state. The data also support the earlier interpretation of the exchange split Δ_2 bands. Since these results are for $T = 100$ K, it is possible that as $T \rightarrow 0$ K some change in the surface magnetic coupling might occur. However, our LEED studies [13] do not yield any evidence of structural changes for $100 < T < 400$ K, i.e., through T_c. This leads us to suspect that the $T = 0$ K nature of the existing theory may not be the cause of the discrepancy in the sign of the surface coupling. It is our hope that these results (both polarization and structure) will provide a more accurate basis for judging if LSDA calculations are yielding meaningful results.

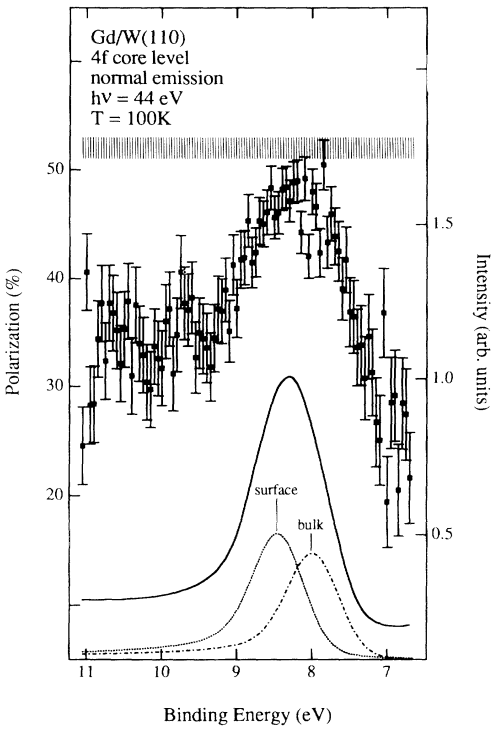

FIG. 3. Intensity and polarization data taken from Gd/W(110). The total intensity is shown separated into the bulk and surface contributions. The shaded bar at the top of the figure delineates the range of the total $4f$ polarization as calculated from the fit line shapes.

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