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Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

Dongqi Li
Argonne National Laboratory, Argonne, Illinois

Jiandi Zhang
University of Nebraska-Lincoln, jiandiz@lsu.edu

M. Onellion
University of Wisconsin, Madison

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P. A. Dowben
Department of Physics, University of Nebraska, Lincoln, Nebraska 68588

Dongqi Li
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

Jiandi Zhang
Department of Physics, University of Nebraska, Lincoln, Nebraska 68588

M. Onellion
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

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Ultrathin Gd films have been studied with constant initial-state spectroscopy (CIS) of photoemission utilizing linearly polarized light of synchrotron radiation. The photoemission cross section of the $5d$ surface state near E_F shows strong photon energy dependence, i.e., sharp peaks in CIS spectra near the Gd $5p_{1/2}$ absorption edge. These peaks originate from resonant photoemission processes involving the occupied $5p$ and unoccupied $5d$ levels of the surface atoms. The symmetry of the unoccupied states were determined experimentally by changing the polarization of light, where p-polarized light excites only to the unoccupied d_{z^2} or $d_{xz,yz}$ states and s-polarized light to all the d states including $d_{x^2-y^2}$ and d_{xy} states. Based on the symmetry assignments, the lower bound of the exchange splitting of the Gd $5d_{z^2}$ surface state can be abstracted, which increases when the thickness of Gd film decreases and reach maximum at the monolayer limit. © *1995 American Vacuum Society.*

I. INTRODUCTION

Extensive studies on the electronic structure of the Gd surfaces have been conducted because of the need to understand the unusual surface magnetic properties of Gd(0001),[1–18] i.e., enhanced Curie temperature of the surface compare to the bulk.[19–23] Such a dramatic effect in surface magnetism is by now known to be connected with the surface electronic structure of Gd, namely, a highly localized surface state at the Fermi level (E_F).[8–15] Magnetism in ultrathin Gd layers is also of interesting at or near the monolayer limit.[24–28] Calculations show an increase in exchange splitting due to further localization of the electrons at low dimensions[10] based upon some preliminary experimental evidence.[4–6] Farle *et al.*, on the other hand, demonstrated that the flat Gd layers epitaxially grown onto W(110) exhibit a scaling of T_C vs thickness.[27] It is therefore necessary to explore how the electronic structure of Gd changes with film thickness down to the monolayer regime, and relate the electronic structure to magnetism. While there are some film thickness dependent studies with photoemission,[4–6,9,12] no thickness dependence information is available for the unoccupied bands. Only for the thicker films is there inverse photoemission data.[7,17] The investigation of the empty states are especially important to assess the surface $5d$ exchange splitting since the minority spin surface state/resonance, the counter part of the occupied one with majority spin, is above E_F at least for the ground state.[10,11,13–15]

While inverse photoemission is a well-accepted technique for measurement of band structure above E_F, adsorption and resonant photoemission can also probe those unoccupied states under some circumstances.[4–6] One can also change light polarization to detect the symmetry character of the unoccupied states.[4,29–32] This symmetry is often difficult to determine in many inverse photoemission setups, making resonant photoemission a valuable tool. In this article, we will present our resonant photoemission studies of Gd ultrathin films down to the monolayer regime. Based upon dipole selection rules in the resonant photoemission process and resulting symmetry assignment of the unoccupied states, we suggest evidence of enhanced exchange splitting of Gd at monolayer.

II. EXPERIMENT

The experiments were carried out at the Synchrotron Radiation Center in Stoughton, Wisconsin, on a 6 m toroidal grating monochromator. Angle-resolved photoemission experiments in both energy dispersion curve (EDC) and constant initial state (CIS) modes were conducted in an ultrahigh vacuum (UHV) chamber equipped with a hemispherical electron energy analyzer and a low-energy electron diffraction (LEED) system.[4] The CIS spectra were taken by scanning the photon energy and electron kinetic energy simultaneously to record the intensity changes of the same initial state, the surface state at E_F in this case.[8–12] The features in CIS are representative of the resonant photoemission processes, where the total photoemission intensity is enhanced by the additional channel of the Gd $5p-5d$ resonance. All the spectra in this work were taken at normal emission, with linearly polarized light from the storage ring incident at 38° or 66° off normal to provide larger portion of light as s or p

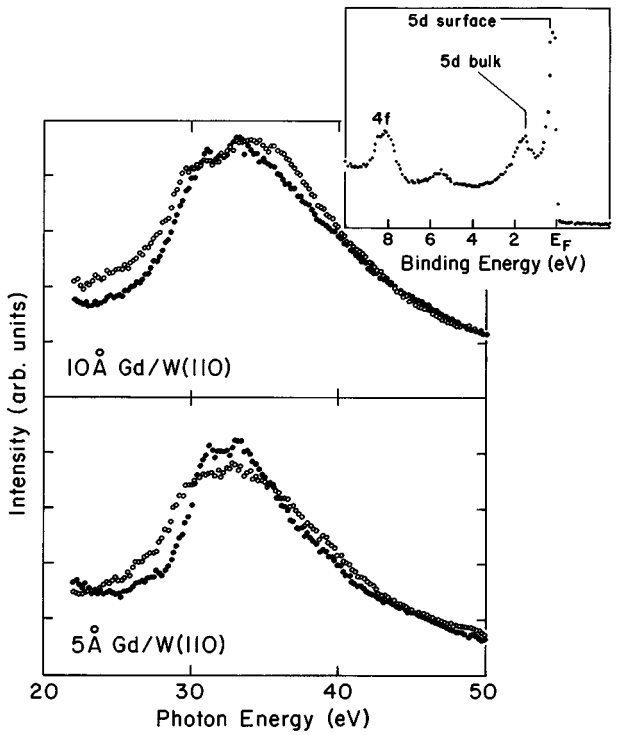

FIG. 1. Constant initial state spectra of Gd films at normal emission with the initial state chosen as the surface state near E_F as indicated in the inset. The circles and the triangles are the spectra taken with more *s*- and *p*-polarized light, respectively. Inset: Photoemission spectrum of Gd film at EDC mode taken at normal emission with photon energy of 33 eV. The Gd $4f$, Δ_1 bulk band and surface state are indicated.

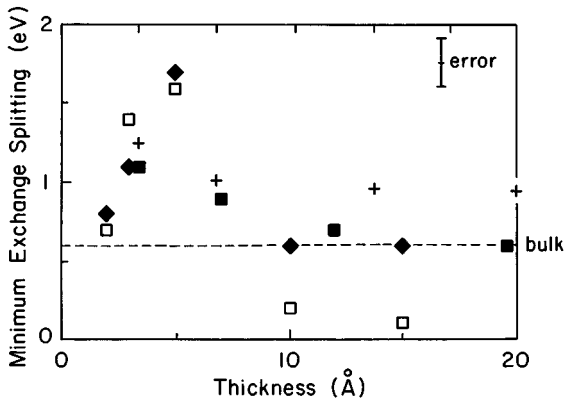

FIG. 2. Minimum exchange splitting as discussed in the text. Filled diamond: Gd/W(110) at 210 K; open square: Gd/W(110) at 295 K; filled square: Gd/Cu(100) at 230 K. The calculated exchange splitting for ferromagnetic surface layers (Ref. 10) are indicated with crosses in the figure for comparison.

polarized, respectively. The combined energy resolution of photoemission was 0.15–0.2 eV and angular resolution $\pm 1.5°$.

Ultrathin Gd films were prepared *in situ* by thermal deposition of Gd onto room temperature W(110)[12] or Cu(100)[4] substrates at a rate of ~ 1 Å/min, as described elsewhere. The pressure during growth was lower than 1×10^{-10} Torr, while the base pressure was $\sim 4-5\times10^{-11}$ Torr. While it is known that subsequent annealing can substantially improve the magnetic properties of Gd/W(110),[26] the effect is not significant for photoemission. All the results of this work are on ''as-deposited'' films to ensure the uniformity and purity of the films. The cleanliness of the substrate and films were checked with valence-band photoemission, and the ordering was confirmed with LEED. Gd/W(111) was ordered, with diffuse LEED spots indicating a Gd(0001) surface, while Gd/Cu(100) films were disordered. The thickness of the films were measured with a quartz–crystal thickness monitor, which is most accurate in terms of the relative thickness changes rather than the absolute thickness. The sample holder could be cooled with liquid nitrogen, and the temperature was measured with a W5%Re/W25%Re thermocouple which was calibrated with a type-*K* thermocouple at a low temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the constant initial state spectra of Gd for two film thicknesses using the Gd(0001) surface state at E_F (indicated in the inset) as the initial state. As indicated by the photon energy range, these CIS spectra were taken around the Gd $5p$ threshold. It is clear that the CIS spectra exhibit well-defined structures. The *p*-polarized spectra show two peaks separated by ~ 2 eV. The similar structures are observed in *p*-polarized spectra if the bulk band at binding energy at 1–2 eV is chosen as the initial state, but which do *not* exist if the initial state energy is chosen at background.

The CIS spectra are strongly dependent on the light polarization. The onset of the *s*- and *p*-polarized spectra, defined as the midpoint of the rising edges, do not match with each other, but instead are shifted by from several hundred meV to 1.7 eV depending on film thickness. As shown in Fig. 2, the energy differences of the onset of the *p*- and *s*-polarized spectra has a strong thickness dependence. The shift between the two has a maximum at around 5 Å (~ 1 ML). The measurements were done for ordered and disordered Gd films, which show similar trend. At low temperature, such a shift remains even at thicker regions of >10 Å), while at room temperature they decrease to almost zero.

In order to understand these data, we first review the resonant photoemission process. In a resonant photoemission process one electron is first excited from the $5p$ shallow core level to the unoccupied $5d$ bands. When those unoccupied states are localized enough, the electron can later decay back via an Auger process, i.e., the super Coster–Kronig transition. It can be written as following:

$$5p^6 4f^7 5d^1 6s^2 \rightarrow 5p^5 4f^7 5d^2 6s^2 \rightarrow 5p^6 4f^7 5d^0 6s^2 + e^-.$$

This provides an additional channel of photoemission with the same initial and final energy states as the direct process. This additional channel exists only when a resonance between the $5p$ and empty $5d$ levels occurs, and should result in an increase in intensity of the surface state at those photon energies. The direct photoemission process, on the other hand, should have a weak, structureless photon energy dependence. The structure in the CIS intensity is therefore mainly from the resonant photoemission process and indi-

cates the relative energy positions of the flat portions of the unoccupied $5d$ states. In addition, the above process is mainly an intra-atomic process. Since the surface state is chosen as the initial state, our measurements mainly probe the electronic structure localized at the surface. As pointed out in previous work, this surface state is highly localized with $d_{3z^2-r^2}(d_{z^2})$ character.[8,9,12]

The light polarization dependence of the CIS spectra can be understood from the dipole selection rule of the resonant photoemission process. The second Auger process involves two electrons, instead of one, and has little symmetry selection. The first process is photon absorption which determines, with the dipole selection rules, the symmetry characters of the unoccupied states that can be reached. For the bands along Γ of the Gd(0001), the point group is C_{6v}. With p-polarized light,

$$A_1(p_z) \rightarrow A_1(d_{z^2}),$$

$$E_1(p_{x,y}) \rightarrow E_1(d_{xz,yz}).$$

Only the unoccupied $5d$ states with d_{z^2} and $d_{xz,yz}$ characters can be reached. With s-polarized light,

$$A_1(p_z) \rightarrow E_1(d_{xz,yz}),$$

$$E_1(p_{x,y}) \rightarrow A_1(d_{z^2}),$$

$$E_1(p_{x,y}) \rightarrow E_2(d_{x^2-y^2,xy}).$$

In this case, all the $5d$ states can be reached. A detailed analysis of the transition matrix, in atomic limit,[32] suggests that pure p-polarized light excites $5p$ electrons into unoccupied $5d_{z^2}$ states four times more and into $5d_{xx,yz}$ states two times more than pure s-polarized light does. S-polarized light, on the other hand, has a larger cross section for the $d_{x^2-y^2,xy}$ states. It is therefore clear that the structures in the p-polarized spectra correspond to the empty states with d_{z^2} or $d_{xz,yz}$ character. Similar selection rules exist even when spin-orbit effects are considered.

Based on these symmetry assignments, the relative position of lowest unoccupied d_{z^2} state can be identified. The onset of the CIS peaks is the threshold of Gd $5p-5d$ resonance, that is, the electrons in the $5p$ core levels are excited to the first dipole-allowed state above E_F. The fact that the onset of p-polarized spectra occurs at higher photon energy than that of s-polarized ones suggests that the density of states near E_F is mainly contributed by the states with $d_{x^2-y^2,xy}$ states, while the d_{z^2} and/or $d_{xz,yz}$ states mainly exist at about several hundred meV to 1.7 eV above E_F.

Realizing that the occupied surface state just below E_F has d_{z^2} character, the energy difference between the onset of $d_{x^2-y^2,xy}$ relative to the d_{z^2}, $d_{xz,yz}$ states defines the lower bound of the exchange splitting of the surface state, which can be further illustrated with a schematic energy level diagram in Fig. 3. We take the energy shift of the onset values for different light polarization as minimum exchange splitting which is less than or equal to the actual exchange splitting. It is therefore possible, as shown in Fig. 2, that the exchange splitting of the surface state changes with Gd thickness and is enhanced at monolayer limit.

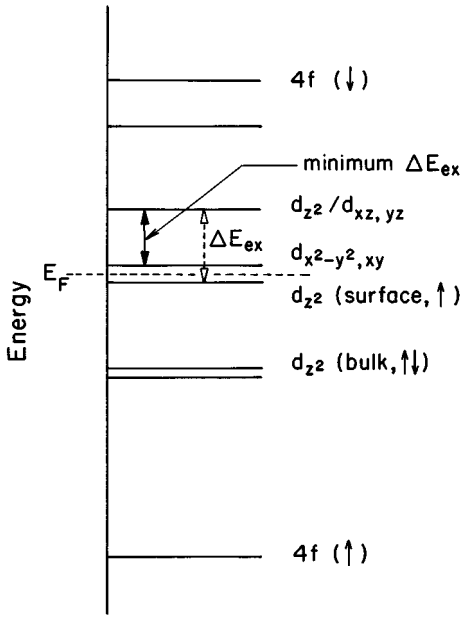

FIG. 3. Schematic of energy levels of Gd. The actual exchange splitting and the minimum exchange splitting are indicated in the figure.

Our results are qualitatively consistent with the theoretical predictions that magnetic systems with lower coordination numbers have larger magnetic moments, and therefore larger exchange splitting.[33] As a comparison, we plot the theoretical values[10] of the exchange splitting for the Gd slabs into Fig. 2, which shows a similar trend that enhances at monolayer limit.

It should be noted that exchange splitting is mainly the indication of local moment which tends to increase when the electrons become more localized, as evidenced by both the exchange splitting and local moment enhancements at surfaces. The maximum of exchange splitting and magnetic moment is reached at the atomic limit. While the increase of magnetic moment *could* lead to enhancement of magnetism, it is not a sufficient condition. The Curie temperature is mainly determined by the strength of exchange interaction, which may or may not scale with the local magnetic moment. Our results on the enhanced exchange splitting therefore do *not* contradict the scaling of T_C with thickness, where T_C decreases at monolayer limit.

IV. CONCLUSIONS

We present CIS studies of Gd ultrathin films, which clearly show strong light polarization and thickness dependence. We discuss the resonance photoemission process and the dipole selection rules to govern it and therefore made symmetry assignments for the CIS features as resonance from $5p$ into the $5d$ states above E_F with different symmetry characters. We postulate that the exchange splitting of the surface state changes with thickness and is enhanced at monolayer limit.

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