Temperature-Dependent Conduction-Band Exchange Splitting in Ferromagnetic hcp Gadolinium: Theoretical Predictions and Photoemission Experiments

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Angle-resolved photoemission is used to determine the temperature-dependent electronic properties of ferromagnetic bulk Gd along Γ-A of the three-dimensional Brillouin zone. The Δ_2 band exchange splitting (0.85 eV) and dispersion (0.5 eV) are in reasonably good agreement with self-consistent local spin-density approximation calculations. The conduction-band magnetic exchange splitting vanishes at the Curie temperature following a conventional power law with a Heisenberg critical exponent. This "Stoner model" collapse of the exchange splitting is in striking contrast to corresponding results observed in transition-metal ferromagnets.

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Gadolinium is a prototype Heisenberg ferromagnet in which the magnetic moments of atomiclike $4f$ states are coupled via exchange with the conduction electrons—the well-known RKKY interaction. Hund's rule applied to the half-filled $4f$ shell of Gd accounts for the $S^{7/2}$ state having no orbital angular momentum ($L=0$) and maximum spin ($J=L+S=\frac{7}{2}$). The conduction band (and valence structure of Gd atoms) is a stable trivalent ($5d6s^2$) configuration, and the measured saturated magnetic moment per atom for Gd metal ($7.63\mu_B$/atom) reveals a significant contribution ($0.63\mu_B$/atom) to the total moment arising from conduction-band spin polarization. Gadolinium has also been considered an important prototype material for testing local-spin-density approximation (LSDA) calculations in rare-earth metals where exchange and relativistic (spin-orbit) effects play important roles [1]. In spite of the recent theoretical progress, important questions remain concerning the accuracy with which the standard LSDA formalism deals with $4f$-conduction-electron exchange effects.

Experimental progress in understanding the electronic and magnetic properties of Gd and other rare-earth metals has been primarily achieved via neutron scattering [2] and de Haas-van Alphen [3] measurements. Photoemission studies [4–11] have achieved some success in elucidating novel electronic and magnetic behavior of rare-earth metals, but the progress has been limited primarily by the difficulty of achieving impurity-free well-ordered crystal surfaces.

One of the first attempts [4] to measure electronic structure of a bulk single-crystal rare-earth metal (Gd) using angle-resolved photoemission met with limited success. The photoemission spectra were found *not* to exhibit the systematic variation of peak positions (binding-energy changes) as a function of photon energy that are understood as manifestations of direct transitions between bulk band states. The absence of bulk band behavior in the photoemission spectra was attributed to strong momentum broadening associated with short electron mean free paths in rare earths (assumed to be 2–3 atomic layers). Similar behavior was encountered in subsequent photoemission studies of Ho [5], Y [6], and Tb [7].

High-quality epitaxial Gd(0001) films can be grown on W(110) [8], and several photoemission studies [9–11], including spin-polarized experiments [11], have been reported. These experiments explored $4f$ excitations [9], discovered a surface state [10], and detected antiferromagnetic coupling between the surface layer and the bulk [11], but have not been successful in elucidating the electronic structure in either the paramagnetic or ferromagnetic state. In this Letter, we report angle-resolved photoemission results for bulk Gd(0001) in both the paramagnetic and ferromagnetic state that exhibit clear manifestations of bulk electronic behavior and establish the relationship between the conduction-band electronic structure and magnetism.

The Gd single crystal used in our experiments was prepared by B. J. Beaudry of the Materials Preparation Center at Ames National Laboratory using techniques described in Ref. [7]. The Gd surface was cleaned *in situ* by repeated cycles of Ne^+ sputtering (500 eV, 10 μA with the sample at $\sim$550 °C) followed by annealing to 680 °C. Our experiments were carried out at the National Synchrotron Light Source using the University of Texas 6-m toroidal grating monochromator [12] and an angle-resolving photoemission spectrometer [13] described previously. Angular and energy resolution of the photoemission spectra reported here are $\pm 0.5°$ and 100 meV, respectively.

Figures 1 and 2 display normal-emission angle-resolved photoemission spectra for Gd(0001) as a function of photon energy at 80 and 300 K, respectively. All spectra in Figs. 1 and 2 exhibit a prominent feature near the Fermi energy that was observed to be very sensitive to surface contamination. The binding energy of this peak is independent of photon energy and the electronic state associated with it lies in a gap of the projected bulk bands. These criteria define a surface state; hence the feature is

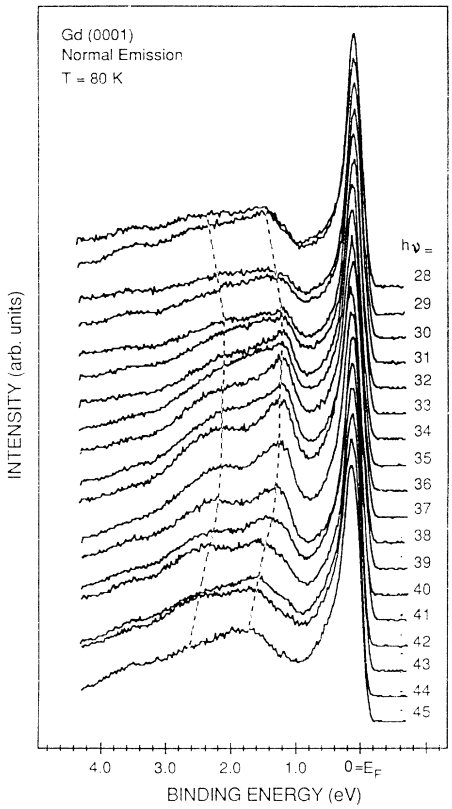

FIG. 1. Normal-emission photoelectron spectra from Gd(0001) for photon energies between 28 and 45 eV at 80 K ($T=0.27T_C$). The extremal peak position is assigned to the critical point Γ_4 of the $\Delta_2^\uparrow$ and the $\Delta_2^\downarrow$ bands.

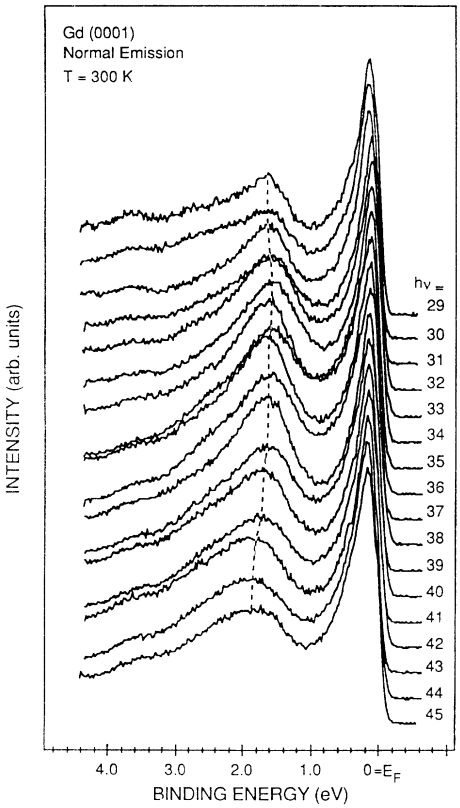

FIG. 2. Normal-emission photoelectron spectra from Gd(0001) for photon energies between 29 and 45 eV at 300 K ($T=1.02T_C$). The extremal peak position is assigned to the critical point Γ_4 of the paramagnetic Δ_2 band.

assigned to the d_{z^2} surface state predicted in the calculations of Wu *et al.* [14] and observed in recent photoemission studies [10] of thin epitaxial Gd films deposited on W(110) (but not reported in earlier studies of bulk Gd [4]).

The broad structure in Fig. 2 exhibits a significant variation of binding energy (~0.4 eV) centered around 1.8 eV as the photon energy is varied from 29 to 45 eV. Figure 1 shows that this structure splits into two distinct structures when the temperature is lowered from 300 K ($1.02T_C$) to 80 K ($0.27T_C$), where $T_C=293$ K is the Curie temperature of bulk Gd. Curve-fitting procedures based on Gaussian-broadened Lorentzian line shapes were used to determine the peak binding energies of each spectrum. The Γ_4 critical point is apparent at the photon energy $h\nu=35$ eV where binding-energy minima occur. Assuming free-electron final states and using an inner potential of 10.8 eV, the direct-transition model [15] is used to obtain a plot of initial-state binding energies along the Δ direction of the Brillouin zone. The reduced data are plotted along with our calculated band structure in Fig. 3. The general behavior of the exchange-split Δ_2 states is in reasonably good agreement with our self-consistent relativistic augmented plane-wave calculations and with other recent calculations [1]. However, the measured bandwidths are narrower (by ~50%) and the measured binding energies are about 0.25 eV closer to the Fermi level than predicted. The magnitude of the exchange splitting at $0.27T_C$, 0.85 ± 0.025 eV, is in excellent agreement both with the low-temperature value deduced from de Haas–van Alphen measurements [3] and with our theoretical value.

Photoemission spectra showing the temperature dependence of the Δ_2 band exchange splitting at fixed $k_\perp$ ($h\nu=38$ eV) are displayed in Fig. 4. The temperature-dependent Δ_2 binding energies were determined by curve fitting assuming equal spectral weights for the exchange-split peaks. At temperatures above $0.7T_C$, two distinct structures are no longer apparent, but continued application of the curve-fitting procedure shows that the component peaks merge at T_C: The width of the composite peak continues to narrow until T_C is reached. Above T_C (even to $T=2T_C$), the peak width and amplitude remain constant. The collapse of the exchange splitting above T_C is in striking contrast to the behavior found in itinerant ferromagnet systems such as Fe and Ni where a finite exchange splitting clearly persists above T_C.

The temperature dependence of the Δ_2 band exchange splitting is shown plotted as a function of reduced temperature T/T_C in the Fig. 4 inset. A conventional power

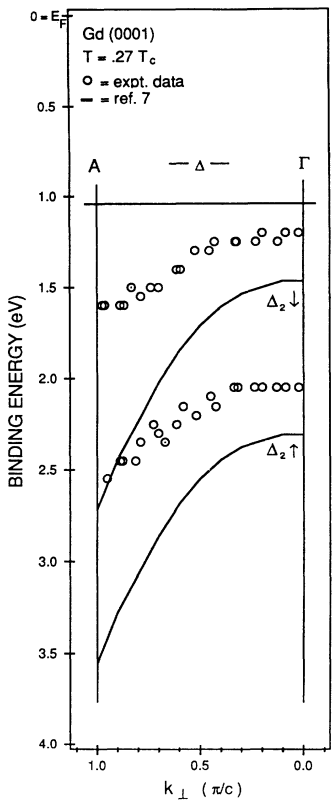

FIG. 3. Comparison of the calculated $\Delta_2^{\downarrow}$ and $\Delta_2^{\uparrow}$ energy bands of Ref. [7] with the experimental data of Fig. 1. The $k_\perp$ position was determined using free-electron final-state bands. The lower branches of the $\Delta_1^{\uparrow}$ and the $\Delta_1^{\downarrow}$ bands from the Γ_1^+ critical point are not shown.

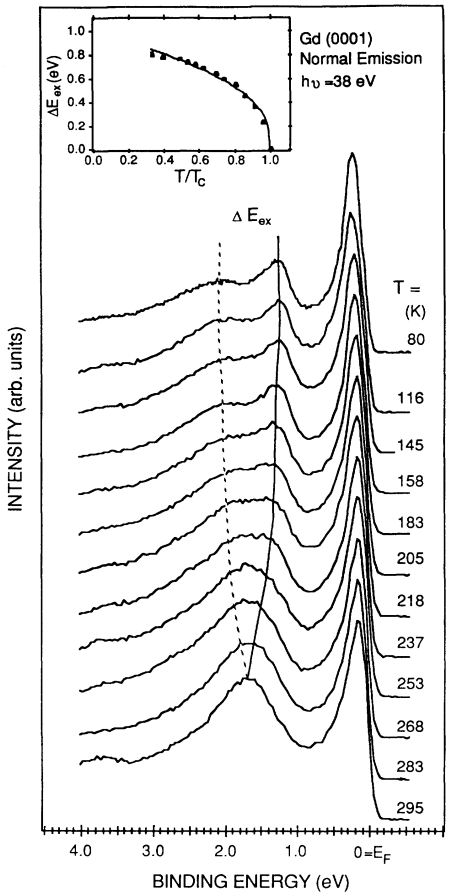

FIG. 4. Temperature dependence of the exchange splitting for the $\Delta_2^{\downarrow}$ and $\Delta_2^{\uparrow}$ energy bands between $T=0.27T_C$ and $T=T_C$ at fixed $k_\perp$ for the photon energy $h\nu=38$ eV. Inset: Plot of peak positions vs reduced temperature, and curve fitted using a power law of the form $\Delta E_{ex}=(1-T/T_C)^{\beta}$. The value obtained for the critical exponent β is 0.378, a value close to the exponent predicted by the Heisenberg model ($\beta\sim0.35$) and also close to the experimental result ($\beta\sim0.40$) for Gd obtained from magnetization measurements [16].

law $\Delta E_{ex}=(1-T/T_C)^{\beta}$ normally used to describe the temperature-dependent saturation magnetization $M_s(T/T_C)/M_s(0)$ is used to fit the experimental points.

Two features of our results merit additional discussion: (1) the collapse of conduction-band exchange splitting at $T=T_C$, and (2) the discrepancies between measured and calculated binding energies. The temperature dependence of exchange splitting and the finite-temperature representations of band structure in transition-metal ferromagnets have been the topic of extensive study and lively debate for decades [17–19]. The more recent work on this problem [18,19] has focused on the relative importance of various conduction-band moment configurations accessible as temperature is varied from $T\ll T_C$ to $T>T_C$. The primary issues have been considered within the framework of two limiting models. The fluctuating local band (FLB) model [18] requires large regions of predominantly aligned moments above T_C, whereas the disordered local-moment (DLM) model [19] requires minimal or no short-range order. Spin- and angle-resolved photoemission studies of both bulk [20] and ultrathin [21] Fe films have failed to detect significant temperature dependence of the exchange splitting for $0.3T_C\leq T\leq T_C$. The temperature-dependent changes in spin-resolved photoemission spectra [22] for Fe (variation of peak amplitude) have been successfully modeled based on a short-range magnetic order theory that bridges the gap between the DLM and FLB models. Corresponding experimental studies [20] of Ni detect a decrease of 40% in the exchange splitting above T_C. The most recent spin-resolved photoemission results for Ni have been successfully interpreted within the FLB model [18] assuming the existence of substantial short-range order.

Mean-field theory [23] (applied to an s-f electron system, like Gd) predicts a splitting of the conduction band into spin-polarized subbands for temperatures below T_C. The calculated exchange splitting is proportional to the average magnetization of the localized moment system. This behavior is precisely what our experimental results indicate, suggesting that in Gd the Bloch wave functions maintain coherence over a distance that is large com-

pared to the $4f$ magnetic correlation length. Evidently, the local exchange field produced by the spin-polarized conduction bands in Gd is too weak to sustain an exchange splitting without a nonzero average $4f$ moment.

Returning to the conduction-band energies determined by our experimental and theoretical studies, we note that the dispersion of the spin-degenerate paramagnetic band ($T > T_C$) appears to be slightly less than that of the exchange-split bands along the Δ direction (0.4 compared to 0.5 eV), and that the experimentally determined binding energies at Γ and A of the exchange-split bands depart significantly from the corresponding calculated energies. Measured binding energies are approximately 20% less at Γ, and the measured bandwidth for the individual Δ_2 subband bands is smaller by a factor of 2, although as previously noted, the calculated and measured exchange splitting (an energy difference) are in excellent agreement.

There are several possible explanations for these discrepancies. Similar effects are well established for d states of ferromagnetic Ni: The d-band width and exchange splitting measured by angle-resolved photoemission are found to be 30% less than the calculated values. This behavior is attributed to self-energy corrections [24] resulting from strong correlation effects. Thus, a self-energy correction that shifts states with d character relative to those of s-p character might help account for the narrower bandwidth observed. It is also interesting to note that the measured exchange splitting is constant along the Δ direction of the Brillouin zone. Our calculations indicate that the d character of the Δ_2 bands increases from approximately 10% at A to 65% at Γ. A second possible origin of the discrepancy between experiment and theory is the novel surface effects associated with Gd(0001). *Ab initio* total-energy calculations [14] of the surface structure of Gd(0001) predict a significant 6% outward relaxation of the top layer. This outward shift (not addressed in our calculations) coupled with lower coordination of surface atoms is consistent with a narrowing of bands. The antiferromagnetic alignment of surface $4f$ states to the bulk $4f$ states [11] could also affect some details of experimental results depending on electron escape depth effects.

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