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Spin-polarized photoemission studies of the exchange splitting of the Gd 5*d* electrons near the Curie temperature

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Spin-polarized photoemission was employed to investigate the temperature dependence of the exchange splitting of Gd(0001) for both the surface state near the Fermi level E_F and the 5*d* bulk bands. The bulk bands at 1–2 eV below E_F show Stoner-like behavior where two peaks with opposite spin polarization shift toward each other as the temperature increases. In contrast, the temperature dependence of the surface state indicates spin-mixing behavior due to fluctuating local moments. These differences are attributed to the degree of itinerancy of the 5*d* electrons in the two cases.

Stoner's model[1] provided the first understanding of itinerant electron magnetism. The model defines an exchange splitting Δ as the energy difference between the majority- and minority-spin bands, and uses this as a characteristic parameter in conjunction with the macroscopic magnetization. While the concept of exchange splitting is now well developed for the ground state, using spin-resolved band-structure calculations, the understanding for finite-temperature magnetism is less mature. Stoner's model predicts a decrease in both Δ and magnetic moment with increasing temperature with both quantities vanishing at the Curie temperature T_C. Such a picture, however, is not realized for transition metals. In those cases, "local band theory"[2–4] and the "disordered local-moment" model[5,6] have been introduced to explain the loss of magnetization at T_C by considering transverse fluctuations of the local moment near T_C. Instead of a collapse of Δ, the energy-split states remain more or less fixed with a "local Δ" (Δ_{loc}) that reflects the existence of a local moment and/or short-range order. But the spin polarization varies with temperature. In contrast to the extensive studies on transition metals, the temperature dependence of the conduction electrons in localized 4*f* systems has not been studied until recently.[7,8] In this case, the same questions emerge concerning the existence of local moments associated with the conduction electrons and short-range order above T_C. The general goal is to understand finite-temperature magnetic properties from a microscopic point of view in order to further advance the theory of itinerant electron magnetism. Here we present angle- and spin-resolved photoemission studies of Gd(0001) at temperatures near T_C. The results unambiguously show that the majority- and minority-spin components of the bulk bands indeed remain spin-polarized and shift toward each other with $\Delta \rightarrow 0$ as $T \rightarrow T_C$. The surface state exhibits a different behavior, where instead of an exchange-splitting collapse, spin mixing occurs, as suggested by the models considering fluctuating local moments.[2–6]

Gd has a large local 4*f* moment of $7\mu_B$, which polarizes the conduction bands and couples to the neighboring moments via a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[9,10] The bulk T_C of Gd is 293 K, which is suppressed in films with thicknesses below ~20–30 monolayers (ML).[11] The surface T_C is reported to be 20–80 K higher than that of the bulk, depending on surface conditions.[12–15] The band structure of Gd has been extensively investigated with photoemission[7,8,16–18] and inverse photoemission.[19,20] In addition to the bulk 5*d* bands at 1–2 eV in binding energy, a magnetic surface state[7,16,20] with majority-spin character[18,21] is observed near E_F. This surface state was shown to be spatially localized both perpendicular and parallel to the surface[7,22] and is responsible for the enhanced surface T_C relative to that of the bulk.[17,22] Temperature effects near T_C have been studied with spin-integrated photoemission for epitaxial Gd films on W(110) (Ref. 7) and Gd single crystals.[8] These studies demonstrate the Stoner-like behavior of the Gd bulk bands[7,8] and suggest that the 5*d* surface state behaves differently.[7] These results were supported by theoretical calculations for Gd.[23,24] However, since the conclusion that the bulk bands exhibit Stoner-like behavior was based on spin-integrated data, it was subsequently challenged. The theory of Sandratskii and Kübler[25] suggests that the local magnetic moment of the conduction electrons (mainly 5*d*) would always exist due to the strong polarization from the local 4*f* moment. But spin polarization and magnetization of the conduction bands would be lost at finite temperature due to global spin-hybridization effects. This controversy can be clarified by characterizing the temperature dependence of the *spin-resolved* conduction bands near T_C with spin-polarized photoemission, as presented in this work. More importantly, the different temperature dependence of the surface state, relative to that of the bulk bands, is investigated.

The thick epitaxial Gd(0001) films[26,27] were prepared *in situ* via thermal deposition onto a W(110) single crystal at room temperature, as described previously.[7,16] The pressure during deposition was $<5\times10^{-11}$ Torr, while the base pressure was 3×10^{-11} Torr. The as-deposited films showed diffuse low-energy electron-diffraction (LEED) spots. The films

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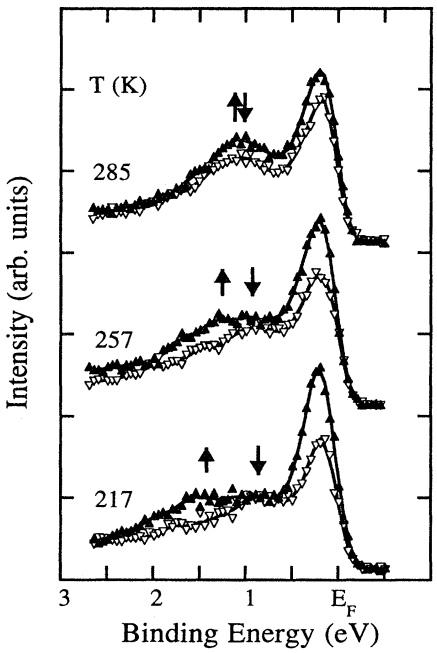

FIG. 1. Spin-polarized photoemission spectra at different temperatures at normal emission. The majority- and minority-spin components are shown with solid (up) and open (down) triangles, respectively. The majority- and minority-spin bulk bands are marked with up and down arrows. The solid lines are to guide the eye.

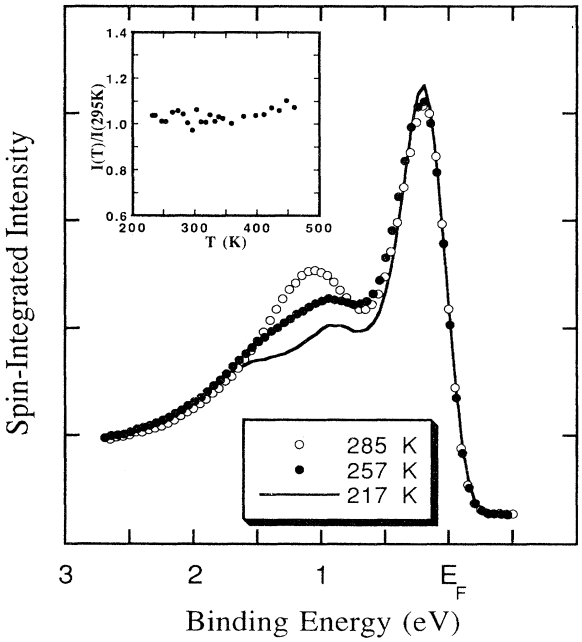

FIG. 2. Spin-integrated spectra from the same measurements as in Fig. 1. The intensities are normalized to the counts above E_F. Inset: normalized intensity of the surface state over a larger temperature range, from Ref. 7.

were subsequently annealed to 780 K to improve their structural order and magnetic properties.[28] The deposition rate was monitored with a quadrupole mass spectrometer and calibrated with the photoemission intensity ratio of the Gd and W core levels. All films were nominally 80 Å thick within $\pm 5\%$. The cleanliness was checked with photoemission, which showed no hydrogen[17] and carbon contamination. At a photon energy ($h\nu$) of 32.7 eV, the oxygen-induced peak at ~ 6 eV was absent from the substrate and as-deposited films. The typical oxygen level of the annealed films was equivalent to ≤ 0.05 L O_2 exposure at room temperature.[29] The sample was cooled down with liquid nitrogen, and was resistively heated with dc current to control the sample temperature between 130 and 350 K. The temperature was measured with a *W*5% Re–*W*26% Re thermocouple, which was calibrated with a type-*K* thermocouple to a precision of ± 5 K.

Spin-polarized photoemission experiments were performed on beamline U5U of the NSLS at Brookhaven National Laboratory. The details of the experimental setup are described elsewhere.[30] The light was incident on the sample at an angle of 65° from the surface normal. The photoemission spectra were taken at $h\nu = 32.7$ eV with a combined resolution of 0.15–0.2 eV. The secondary-electron spin polarization was measured with $h\nu = 69.5$ eV. The electrons were collected at normal emission. The sample was biased to -30 V to minimize the effects of the stray field caused by the sample heater. The samples were magnetized in-plane with a pulsed field, and the measurements were taken in the remanent state.

Figure 1 shows three typical spin-polarized photoemission spectra taken at different temperatures from two nominally identical Gd films. The bulk bands at 1–2 eV binding energy show two features with majority- and minority-spin character, respectively, as marked in Fig. 1. With increasing temperature, the spin polarization of the two bulk-band peaks is retained, while Δ decreases and approaches zero at T_C. This implies that $\Delta(T)$ of the $5d$ bulk band $[\Delta_b(T)]$ is indeed well defined even at finite temperature and has a Stoner-like behavior.

It is apparent that the surface state near E_F is spin polarized, and the polarization is in the same direction as that of the $4f$ levels (not shown) and the bulk majority-spin feature. Thus, the surface state has majority-spin character, and the surface and bulk spins are mainly ferromagnetically coupled, as reported previously.[14,18,21] The question is whether the surface state Δ (Δ_s) collapses at the surface T_C. The spin polarization of the surface state decreases with increasing temperature, while its binding energy remains fixed within experimental error, as seen in Fig. 1. Figure 2 shows the spin-integrated spectra from the same measurements shown in Fig. 1; all spectra were normalized to the background signal above E_F. It is immediately apparent that the surface-state features at the different temperatures overlap with each other. This means that not only the binding energy, but also the intensity of the surface state, remain fixed near T_C even though the spin polarization changes dramatically. In the inset, we show the surface-state intensity for a sample from Ref. 7. It is clear that the intensity is constant over a large temperature range well below and above the surface T_C. The constant binding energy and intensity of the surface state suggest that there is no state crossing E_F at the zone center (normal emission) during the magnetic phase transition. The

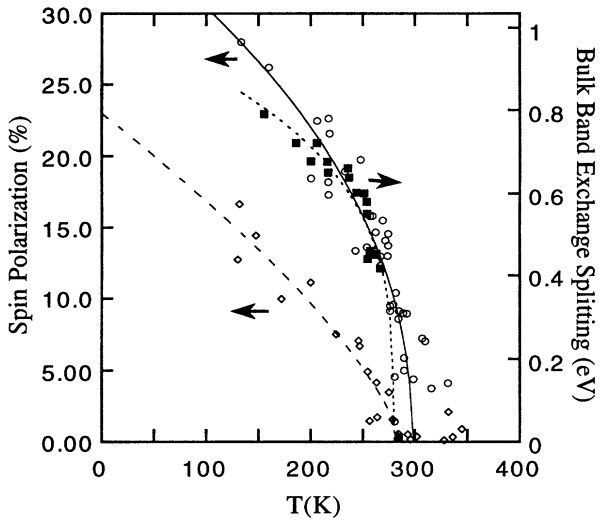

FIG. 3. Temperature dependence of the bulk-band exchange splitting (squares), and the spin polarization of the surface state (circles) and secondary electrons (diamonds). The lines are to guide the eye.

dramatic polarization change of the surface state across T_C, therefore, does *not* originate from the collapse of its exchange splitting, but instead, follows spin-mixing behavior expected for an itinerant electron system with transversely fluctuating local moments.[2–6] It was shown previously that the width of the surface state increases linearly with temperature,[7] which is also consistent with spin mixing, but not with state(s) crossing E_F.

Figure 3 shows the temperature dependence of the spin polarization of the surface state, the bulk-band exchange splitting, and the spin polarization of the secondary electrons, measured from several nominally identical samples. These quantities reflect the magnetic properties, respectively, of purely the surface, purely the bulk, and a combination of the two. Some of the Δ_b values were obtained directly from fitting spin-polarized spectra, while most of the values were derived from the spin-integrated spectra by fitting to three Gaussian peaks after subtraction of an inelastic background. Two of the peaks that correspond to the spin components of the bulk bands were equally weighted. The simple Gaussian line shape was chosen to minimize the adjustable parameters and is justified by the relatively large instrumental broadening (Gaussian) as compared to the intrinsic Lorentzian linewidth. The Δ_b can be determined by such fitting procedures only when its value is larger than the energy resolution, and it is therefore difficult to characterize near T_C. The spin-polarized spectrum at 285 K (Fig. 1) shows $\Delta_b = 0$, indicating that Δ_b indeed approaches zero near T_C. Nevertheless, the surface state and secondary-electron spin polarization, and the bulk $5d$ band exchange splitting all show strong temperature dependences, attributable to the changes in the magnetization at the surface and in the bulk.

A comparison of the data from the bulk bands and surface state clearly demonstrates the differences in behavior at finite temperatures. The bulk bands show a temperature-dependent exchange splitting that approaches zero at T_C at least at $\bar{\Gamma}$. The off-normal part ($k_\parallel = 0$) of the bulk bands also show significant temperature dependence, though different from that of the zone center.[7] Overall, the behavior of the bulk band suggests the change in magnetic moment of the bulk $5d$ electrons since the moment is determined by the relative occupation of the local spin-up and spin-down states. Himpsel showed an empirical relation of scaling between Δ and the magnetic moment (1 eV in Δ corresponds to $\sim 1\mu_B$ in magnetic moment) for $3d$ electrons,[31] which also roughly holds for Gd $5d$ when comparing the surface and bulk at ground state.[32] The change in Δ_b therefore suggests that the local $5d$ moment in the bulk also decreases with temperature and approaches zero at T_C. This behavior is similar to that of Stoner's mean-field model,[1] where both Δ and the local moment of the itinerant electrons decrease with temperature. For the surface state, Δ_s becomes ill-defined at finite temperatures due to the different spin components gradually becoming hybridized as a consequence of the loss of long-range order. Such behavior is similar to that of the models for transition metals.[2–6] In such models, a local magnetic moment and $\Delta_{\rm loc}$ exist and remain more or less fixed in energy with temperature due to a finite local moment and/or the short-range order of the itinerant electrons. For the surface state of Gd, this $\Delta_{\rm loc}$ does not go to zero at the surface T_C based on the present data. This suggests a finite local $5d$ moment at the surface even above T_C. It should again be noted that even though comparisons with models for itinerant ferromagnets are made, Gd is different from the transition metals since its $5d$ electrons are polarized by the local $4f$ moment.

The difference between the surface state and the bulk-band behavior of Gd can be qualitatively understood from the fact that while they are both polarized by the $4f$ moments, the surface state is relatively localized compared to the bulk bands. This surface state is unusual in that it is known to be highly localized even *within* the plane, based on the flatness of the experimental and calculated dispersion curve.[7,16,32] Such localization helps these $5d$ electrons to remain locally polarized by the local $4f$ moment even after the $4f$ moments lose their long-range order at T_C. The more itinerant bulk-band electrons, however, are more likely to experience the collective polarization from the $4f$ moments within a larger range as a mean-field effect, and therefore the bulk $5d$ moment and the Δ_b vary with the magnetization. To be more precise, the electrons in the surface state remain phase coherent on a length scale less than the magnetic correlation length, while the opposite is true for the bulk bands. Our experimental results therefore do not directly prove or disprove the existence of the short-range order of Gd, but instead provide information on its relative spatial extent (magnetic correlation length) vs electron coherence length. From the band dispersion of the bulk bands and surface state, we can estimate the electron phase coherence length as $l \approx \sqrt{w/k_B T_C}\, a$, where w is the bandwidth.[33] Given the in-plane lattice parameter $a = 3.64$ Å and estimating the bandwidth as being ~ 1.5 eV,[7,22] $l \approx 28$ Å for the bulk band, and should be much shorter for the surface state. This also implies that the upper limit of the extent of short-range order in the bulk is ~ 28 Å.

Our photoemission experiments only detail the behavior of one spin component of the surface state. The counterpart with minority spin is expected to be unoccupied.[22] Inverse

photoemission results[19] at room temperature show a surface state just above E_F, and another possible surface state/resonance about 1 eV above E_F. A temperature-dependent inverse photoemission study[20] claimed that a surface state crosses E_F near T_C, based on the loss of intensity of one of the fitting peaks in a multiple-peak fitting of the spectra. Our present results clearly show that no state crosses E_F near T_C, indicative of a nonzero Δ_{loc} and a finite local moment above T_C. This does not, however, exclude the possibility that the Δ_{loc} could change with temperature to some degree.[25,34,35] Strictly speaking, we cannot completely rule out the possibility that near T_C, equal portions of the minority- and majority-spin states shift across E_F to keep the intensity of the occupied surface state constant, though it is harder to reconcile with all the existing results. It would be interesting in the future to conclusively identify the minority-spin surface state/resonance above E_F and to further investigate the issue with spin-polarized inverse photoemission at different temperatures.

In principle, the bulk and surface T_C values can be determined simultaneously from the temperature dependence of the Δ_b and the surface-state spin polarization, respectively. We find from Fig. 3 the values of the bulk $T_C = 283 \pm 10$ K and the surface $T_C = 297 \pm 10$ K. The large error bar is because it is difficult to extract accurate values of Δ_b from the spin-integrated spectra, and the spin-polarized spectra provide limited data points in the transition region. From the spectrum taken at 285 K (Fig. 1), Δ_b is 0 within the resolution limit, while the spin polarization of the surface state is clearly nonzero. Our results, therefore, are consistent with a higher value for the surface T_C than for the bulk.[12,14] It should also be noted that our experiments involve only in-plane magnetization. Since the surface moments are canted out of the surface plane,[14,18] it is also possible that the surface moments rotate toward the surface normal above the bulk T_C, making it even more difficult for us to identify the surface Curie temperature.

In conclusion, we have investigated the spin-resolved electronic structure of Gd(0001) at different temperatures. The bulk bands exhibit a mean-field Stoner-like behavior indicating a vanishing local $5d$ moment. The surface state shows spin mixing with increasing temperature, which correlates with the more localized nature of this state.

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