Temperature Dependence of the Exchange Splitting of the Surface State on Gd(0001): Evidence against Spin-Mixing Behavior

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We report on angle-resolved photoemission (PE) and inverse PE studies of Gd(0001) in the temperature range 60 to 400 K. The results show that with increasing temperature both the occupied and the unoccupied parts of the d-like surface state at $\overline{\Gamma}$ shift towards the Fermi level. This rules out a pure spin-mixing behavior as claimed recently on the basis of spin-resolved PE data. Instead, the temperature variation of the surface-state exchange splitting is Stoner-like, with an enhanced surface Curie temperature; nevertheless, a small residual splitting above T_C cannot be ruled out. [S0031-9007(96)01417-2]

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Gd metal, as a prototypical ferromagnet with local moments, has attracted considerable interest in recent years. The large local spin-only magnetic moments of the half-filled quasiatomic $4f$ shell, which couple magnetically via RKKY interaction, give rise to ferromagnetic order with a bulk Curie temperature of $T_C^b = 293$ K. For the topmost surface layer, an enhancement of T_C by up to 60 K has been reported [1–3]. In this context, the discovery of an occupied surface state with d_{z^2} symmetry, localized in the topmost surface layer of Gd(0001), has been essential, since it might be responsible for the enhanced magnetic coupling at the surface [4–7]. It has also been shown that the occupied part of the surface state has mostly majority-spin character at temperatures well below the surface Curie temperature T_C^s [8]. Furthermore, the magnetization of the surface layer of Gd(0001) was found to be ferromagnetically oriented with respect to the bulk [8,9], with the possibility of a slight canting for relatively thick films [3].

Photoemission (PE) studies revealed a temperature-dependent exchange splitting of the bulk bands of Gd in the ferromagnetic phase, which disappears at T_C^b, in agreement with the Stoner-like behavior expected for itinerant band states [10,11]. On the other hand, a spin-mixing behavior has been suggested for the surface state [12], based on spin-resolved PE results, in agreement with theoretical considerations for localized states [13,14]. These include the study of the temperature behavior of band states of bulk Gd, which led to the result that the exchange splitting of the more localized states with d character should be quite independent of temperature, while the more extended s-derived states were found to exhibit a Stoner-like behavior [14]. In the former case, only the spin polarization was found to decrease with temperature. These theoretical findings support an interpretation of the experimental observations in terms of a Stoner-like behavior of the bulk bands and a spin-mixing behavior of the strongly localized surface state [11,12].

In the present Letter, high-resolution PE and inverse photoemission (IPE) results on Gd(0001) are presented, and it will be shown on the basis of a combined analysis of these data that the temperature variation of the exchange splitting of the surface state is qualitatively similar to that of bulk-band states. In particular, a Stoner-like decrease of the exchange splitting with increasing temperature is observed, in contrast to conclusions from previous lower-resolution PE studies.

The PE experiments were performed at the TGM-5 undulator beamline of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using a VSW-ARIES electron spectrometer with an angular resolution of $\pm 1°$ and a total-system energy resolution of 60 meV (FWHM). The metal films were prepared by depositing $\cong 80$ Å of Gd on W(110) in a chamber with a base pressure below 2×10^{-11} mbar that rose to $\cong 8 \times 10^{-11}$ mbar during evaporation. Subsequent annealing led to well-ordered films with sharp hexagonal LEED patterns and no detectable contamination as monitored by PE at $h\nu = 40$ eV. These Gd(0001) films exhibited a well-pronounced and narrow surface state close to E_F [see Fig. 1(a)]. The samples could be cooled to 20 K with a closed-cycle He refrigerator, and the temperature was measured to an accuracy of ± 10 K with a $W_{76}Re_{24}/W_{95}Re_5$ thermocouple directly attached to the W crystal. Angle-resolved IPE spectra were recorded with a home-built spectrometer equipped with a toroidal-grating monochromator and a Pierce-type electron gun [15]. In IPE, the total-system resolution was 0.3 eV (FWHM).

Figure 1 displays angle-resolved PE spectra of Gd(0001) taken at normal emission. An overview of the valence-band emission, taken with 40-eV photons, is presented in Fig. 1(a); it includes the $4f$ emission at $\cong 8.5$-eV binding energy (BE), with resolved bulk (b) and surface (s) signals [16]. The feature B around 2-eV BE represents the exchange-split bulk Δ_2 bands [10]. The pronounced narrow peak S close to E_F stems from the occupied part of the surface state; analogous surface

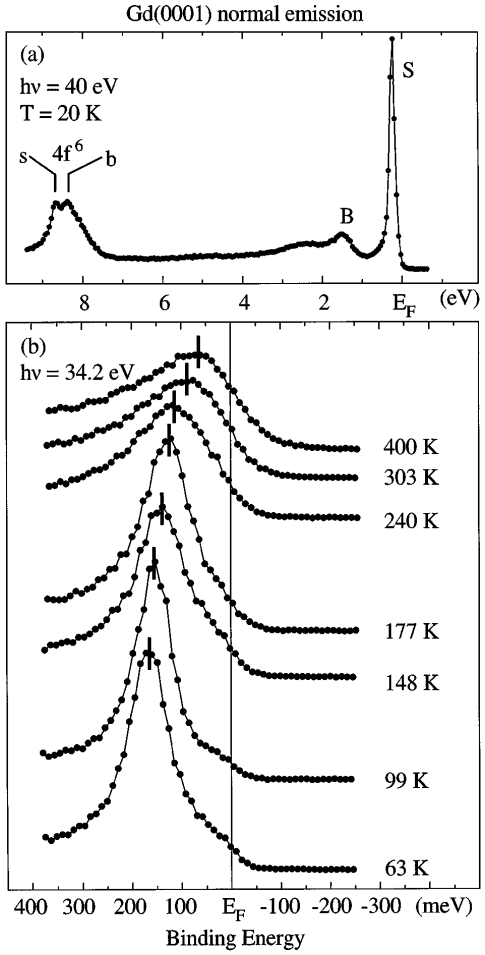

FIG. 1. Angle-resolved normal-emission PE spectra of Gd(0001): (a) Overview of the valence-band region. B (b) and S (s) denote emissions from the bulk and the surface, respectively. (b) Surface-state spectra at various temperatures.

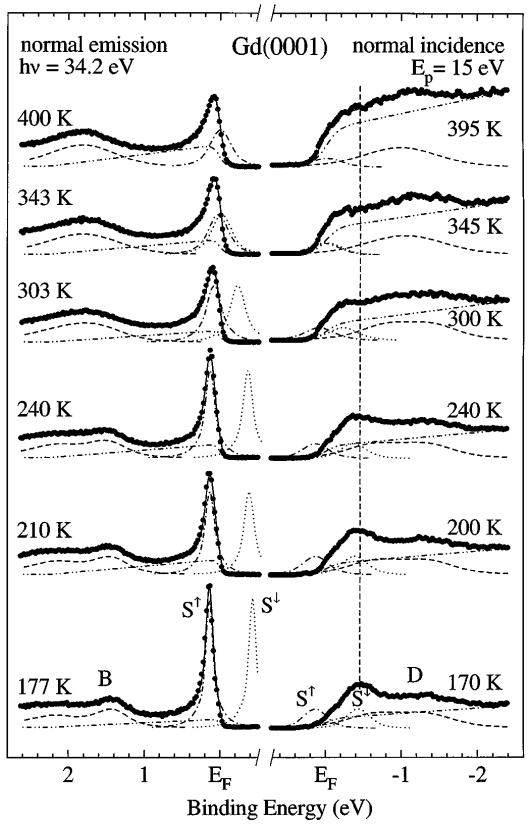

FIG. 2. PE (left) and IPE (right) spectra of Gd(0001) taken at various temperatures. The solid curves through the data points represent the results of simultaneous least-squares fits for a given temperature. $S^{\uparrow}$ (dash-dotted) and $S^{\downarrow}$ (dotted) indicate the two exchange-split surface-state components employed in the fits; B and D (dashed) represent the exchange-split $5d$ bands. Note the sizable shift of $S^{\downarrow}$ in the IPE spectra.

states have been reported for close-packed surfaces of essentially all lanthanide metals [7,16–18]. Figure 1(b) shows the temperature dependence of the surface-state emission, with the spectra normalized to equal intensity of feature B. At low temperatures, the surface state is well separated from E_F, with a BE of 170 meV at 63 K. The BE of S can be accurately determined for temperatures up to $\cong 240$ K; at higher temperatures, this becomes increasingly difficult due to the thermal broadening as well as the fact that the peak moves towards E_F. To overcome these difficulties, the unoccupied part of the surface state was additionally studied by IPE, allowing a combined analysis of the sets of PE and IPE spectra.

IPE spectra of Gd(0001), recorded with a primary-electron energy of $E_p = 15$ eV in normal incidence, are presented in Fig. 2 (right panel), together with PE spectra at approximately equal temperatures (left panel). Note that both series of angle-resolved spectra represent the electronic structure at the $\overline{\Gamma}$ point of the surface Brillouin zone. The two series of spectra are dominated by the occupied (PE) and unoccupied (IPE) parts of the surface state, separated by an exchange splitting of 570 ± 10 meV at 170 K. In addition to the surface-state peak, the IPE spectra contain feature D at $\cong 1.5$ eV above E_F, which has been interpreted as due to transitions to unoccupied $5d$ band states in the topmost surface layer [6], in analogy to the Δ_2-band feature B in PE.

Even though the assignment of components $S^{\downarrow}$ and D in the IPE spectra is not straightforward, since the exchange splitting of D is not resolved, it follows from a consistent description of the whole temperature series of IPE spectra [6]. One could argue that peak D might be the minority-spin part of the surface state. Such an interpretation of the IPE spectra is not consistent, however, since one would then need a completely different origin for component $S^{\downarrow}$. At low temperatures, $S^{\downarrow}$ is too far away from E_F to represent the unoccupied tail of $S^{\uparrow}$, which dominates the PE spectra. Peak $S^{\downarrow}$ is also highly sensitive to oxygen contamination [6], similar to $S^{\uparrow}$ in the PE spectra, revealing that it is surface derived. Furthermore, the analogous PE and IPE spectra of La(0001) show that (i) the occupied and unoccupied parts of the $5d$ bands have similar energies as in Gd, and (ii) the surface

state is directly located at E_F [19]. Since La metal is nonmagnetic and has no $4f$ moment, exchange splitting and even local splitting can be ruled out. It is therefore highly plausible to assign component $S^{\downarrow}$ to the minority part of the exchange-split surface state, although its spin character has not been determined [20] and the observed exchange splitting is somewhat smaller than theoretically predicted [5].

With increasing temperature, $S^{\downarrow}$ shifts towards E_F, and above 200 K it gets increasingly more difficult to determine its energy from the IPE spectra alone. Therefore the energy of $S^{\downarrow}$ was derived from a simultaneous fit of the PE and IPE spectra for a given temperature. In the PE case, a set of two asymmetric Lorentzians was used to simulate the bulk emission (B), while in the IPE case, the $5d$ bands could be described by two symmetric Lorentzians (dashed subspectra). To both spectra backgrounds were added (dash-double-dotted) to account for inelastically scattered electrons as well as nondirect transitions. The surface-state emission in PE and IPE was simulated by *one* set of two identical symmetric lines ($S^{\uparrow}, S^{\downarrow}$), assumed to be the sum of a Gaussian and a Lorentzian function. The resulting line shapes were multiplied by a Fermi function and convoluted by a Gaussian to account for finite experimental resolution.

The fit results are given by the solid lines through the data points. It is obvious that the PE and IPE spectra are well described by a continuous collapse of the surface-state exchange splitting. In this way, the energies of components $S^{\uparrow}$ and $S^{\downarrow}$ could be derived quite accurately even for temperatures above 200 K. Note that the exchange splitting of the bulk-band feature B in PE collapses around 300 K, while a small residual splitting remains in case of the surface state. Feature D also shows a residual splitting at room temperature, which is due to the surface character of this emission [6].

The results of this analysis are summarized in Fig. 3(a), which displays the BE of components $S^{\uparrow}$ and $S^{\downarrow}$ relative to E_F; for PE, data points at additional temperatures were included. The resulting exchange splitting of the surface state, Δ_{ex}, is plotted in Fig. 3(b) for those temperatures where both PE and IPE spectra have been measured. The temperature dependence of Δ_{ex} indicates an enhanced T_C in the topmost surface layer. Because of the large error bars in the critical-temperature range, an accurate value of T_C^s, however, cannot be derived from the data in Fig. 3. If one describes the temperature dependence of Δ_{ex} by a power law and assumes that the splitting disappears at T_C, an estimate of $T_C^s \cong 345$ K can be given, in fair agreement with a recent result from a secondary-electron study [3].

The temperature dependence of the surface-state exchange splitting found here contradicts conclusions drawn by Li *et al.* [12], who claimed a spin-mixing behavior. This was based on their spin-resolved PE observation that the surface state does not shift with temperature, but rather loses spin polarization. They also claimed to have seen a constant spin-integrated intensity, which would be hardly understandable for a surface state crossing E_F. Their conclusions, however, could have been influenced by the lower energy resolution in their study, insufficient to observe the small BE shifts of the occupied surface state reported here. The observed loss is spin polarization of the surface state with increasing temperature can be explained on the basis of the present results: With $S^{\uparrow}$ and $S^{\downarrow}$ being close to E_F, the shifts observed here with increasing temperature lead to a depopulation of $S^{\uparrow}$ and an increasing population of $S^{\downarrow}$. Since components $S^{\uparrow}$ and $S^{\downarrow}$ were not resolved in the work of Li *et al.*, it is plausible that only a decrease of the net polarization plus a constant spin-integrated intensity of the surface state was seen in PE.

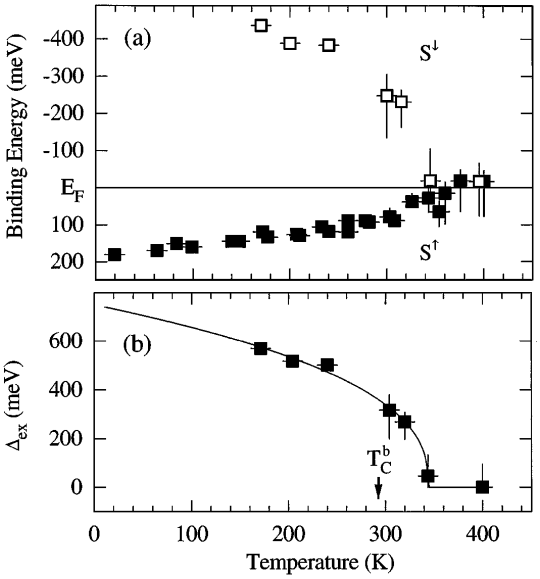

FIG. 3. (a) Binding energies of components $S^{\uparrow}$ (■) and $S^{\downarrow}$ (□), and (b) surface-state exchange splitting, Δ_{ex}, as a function of temperature. The solid line through the data points represents the fit result based on a Stoner-like mean-field dependence.

Even though the temperature dependence of Δ_{ex} of the surface state has been found here to be qualitatively Stoner-like, a residual splitting up to 100 meV may remain above T_C, indicated by the relatively large error bars in Fig. 3. Since the spin characters of components $S^{\uparrow}$ and $S^{\downarrow}$ have not been measured here, some depolarization, in addition to the observed energy shifts, cannot be ruled out. A pure spin-mixing model, however, which predicts an almost constant exchange splitting [14], is definitely inconsistent with the observed decrease of Δ_{ex} from $\cong 570$ meV at 170 K to ≤ 100 meV at 350 K. The bulk-band states of Gd were shown on the basis of spin-integrated [8,11] as well as spin-resolved [10,12] PE studies to exhibit a Stoner-like behavior, with the exchange splitting disappearing at $\cong 300$ K. Again, the resolution in these studies was not sufficiently high to rule out a small residual splitting above T_C^b of the

order of 50 meV. The present PE data are consistent with such a small residual splitting. We therefore conclude that the bulk-band states and the surface state of Gd(0001) behave qualitatively similar: With increasing temperature, the exchange splittings of both decrease in a Stoner-like fashion, with some uncertainty concerning the sizes of the residual splittings above the respective Curie temperatures.

We finally address the question of temperature-induced BE shifts of nonmagnetic origin. As is well known from angle-resolved PE experiments, the BE of the Tamm-like surface states on Cu(100) and Cu(111) exhibit distinct temperature dependences [21,22], with Be shifts of 0.16 meV/K in the latter case, which have been interpreted as initial-state energy shifts caused by thermal narrowing of the gap of the projected bulk-band structure [22,23]. An analogous mechanism may well contribute in the present case of the Gd surface state; it cannot, however, account for the far larger shifts observed here, which amount to $\cong 400$ meV in IPE for a temperature difference of 200 K. Furthermore, the shifts in IPE and PE have opposite signs, which cannot be explained on the basis of an initial-state energy shift. The shift of the center of gravity of the exchange-split surface state towards lower energies, amounting to $\cong 140$ meV from 170 and 400 K, might be due to this mechanism.

In summary, the surface state on Gd(0001) reveals an exchange splitting that decreases significantly with increasing temperature and collapses only at a temperature well above T_C^b. Although a small residual splitting above T_C cannot be ruled out, the data presented here are in agreement with an essentially Stoner-like behavior as found for bulk-band states. This is in contrast to theoretical considerations, which would favor a spin-mixing behavior for the localized surface state. These results demonstrate the need for an improved theoretical description of the magnetic properties of band states with varying degrees of localization in local-moment magnetic systems.

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