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The effect of magnetic ordering on the temperature dependence of the gadolinium bulk band structure

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Abstract. A temperature-dependent shift of the gadolinium bulk bands is observed at temperatures across the gadolinium bulk and surface Curie temperatures. The temperature dependence of the bulk band structure is sensitive to the position in k-space. This shift of the gadolinium band structure is suggested by recent quasiparticle calculations for the bulk.

The band structure of metals, in ferromagnetic materials, is dependent upon magnetic ordering [1–11]. Such temperature dependence may be qualitatively understood from simple pictures such as the mean field Stoner model [12] though numerous complications exist. The temperature dependence of the exchange splitting in nickel, for example, has been investigated [1–4]. The exchange splitting is seen to persist for temperatures above T_c, indicative of the existence of short-range magnetic order [13]. Studies of magnetic surface states do provide indications that surface magnetic properties differ from those in the bulk [3] although for some transition metals, like nickel, the surface states have decay lengths of one to three layers into the bulk [14, 15].

A study by Weller and co-workers [8] demonstrated that the surface layer of Gd(0001) is coupled antiferromagnetically with the bulk and that the surface possessed a Curie temperature of 315 K, 22° higher than the bulk Curie temperature of 293 K [8–11]. This suggests a remarkable magnetic coupling between the surface and the bulk. One indication of the different surface and bulk magnetic properties is manifest in the band structure as a magnetic surface state that appears in the vicinity of $\bar{\Gamma}$ which has been studied experimentally [16, 17] and theoretically [18, 19].

There has also been considerable interest in investigating the temperature dependence of the rare earth magnetization [8–11, 20–24] and electronic band structure [7, 25, 26], since the rare earth ferromagnets are considered local spin systems, in contrast with transition metals which are itinerant ferromagnets. Most photoemission studies of the temperature dependence of the rare earth metal valence band structure have not produced significant results. In this work, we demonstrate that studies similar to those undertaken for nickel [3, 4] are possible for Gd(0001). A large exchange splitting temperature dependence is surprising in a local spin system.

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Gadolinium films deposited on W(110) have been studied by a number of groups, and several studies have established that the films (thicker than one monolayer) adopt the crystal structure of bulk gadolinium with the (0001) face parallel with the W(110) surface (i.e. the *c*-axis lies along the surface normal) [27–29]. This property of gadolinium films deposited on W(110) permits us to investigate crystalline gadolinium films of exceptional purity. Our experiments were performed on a 6 m toroidal grating monochromator and a grasshopper monochromator at the Synchrotron Radiation Center. Depositions were carried out by methods established for providing clean films [30] in a vacuum system with a base pressure of 8×10^{-11} Torr. LEED studies were undertaken to confirm the crystalline order and orientation of the gadolinium films. The sharp hexagonal LEED patterns, for films thicker than one monolayer, are consistent with earlier results [27–29]. We did not observe any structural changes of the films over the temperature range from 300 K to 200 K. The temperature was determined with a W–WRe thermocouple with an accuracy of 5 K as a result of systematic errors which are the greatest source of temperature uncertainty. The experiments were carried out in the short period of time following evaporation of the film to ensure that contamination did not influence the results, since surface magnetic properties are sensitive to sample preparation [8]. The data were taken in an angle resolved photoemission system equipped with a hemispherical electron energy analyser, described in detail elsewhere [30], under conditions that provided a resolution better than 100 meV.

In figure 1, photoemission spectra of Gd(0001) grown on W(110) are shown for normal emission ($k_{11} = 0, \bar{\Gamma}$ of the surface Brillouin zone). The spectra are taken with the temperature decreasing from 510 K to 200 K. The sharp feature near the Fermi energy does not disperse with photon energy (at normal emission) and has been identified as a magnetic surface state [18, 19].

The feature with a binding energy of about 1.8 eV less than the Fermi energy at 300 K does disperse with photon energy and is believed to be the bulk-like band which develops with increasing thickness [17] and resembles a pair of bulk bands observed by Himpsel and Reihl [31] for single-crystal Gd(0001) and Wu and co-workers [32] for Tb(0001) along Γ to A of the bulk Brillouin zone. Both gadolinium 5d band features disperse with k_{11} (off normal emission) in a manner consistent with the band structure calculations of Wu and co-workers [18, 19] as seen in figure 2.

By cooling the Gd(0001) film from a temperature well above both the bulk Curie temperature (T_{cb}) of 293 K, and the surface Curie temperature of (T_{cs}) of 315 K [8, 11], to a temperature below both Curie temperatures, a clear shift in the gadolinium 5d bulk bands is observed as seen in figure 1. The binding energy shift is reversible even with repeated cycling of temperature between 200 K and 300 K. The changes with temperature in the photoemission feature attributable to the bulk bands include changes not only of the binding energies, but also of the feature full width at half maximum, with the minimum half width of the feature at about 0.8 eV observed at temperatures around 310 to 340 K, the maximum of this temperature dependent binding energy. The temperature dependent shift of the bulk bands is, nonetheless, strongly dependent upon emission angle (i.e. variation in k_{11} as seen in figure 2) and photon energy (variation in $k_{\perp}$).

The surface state is not observed to shift by more than 50 meV in binding energy across T_{cb}, or indeed over the entire temperature range investigated. The half width of the surface state is observed to slowly increase with increasing temperature (as seen in figure 1). The absence of substantial change in the surface state binding energy

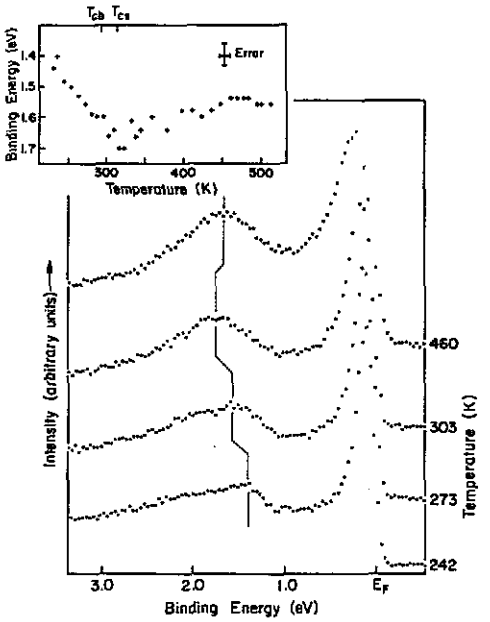

Figure 1. Photoemission spectra of 30 Å gadolinium films on W(110). Photoelectrons were collected at normal emission ($\bar{\Gamma}$) and the light incidence angle was 34° off the surface normal (s + p polarized light). The shift in the bulk bands is indicated. The photon energy was 33 eV. The plotted temperature-dependent binding energies of the bulk bands, derived from spectra as shown above (for a 33 eV photon energy) is shown in the inset.

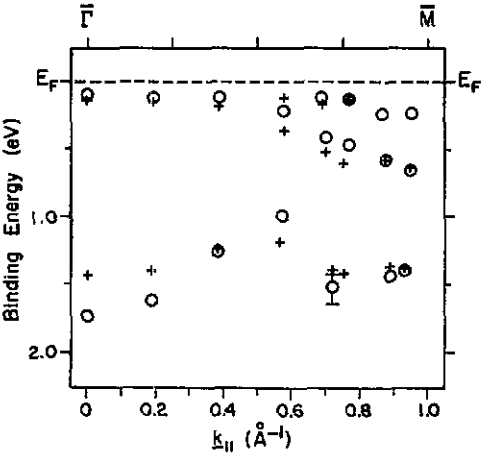

Figure 2. The experimental band structure from $\bar{\Gamma}$ to $\bar{M}$ of the surface Brillouin zone from spectra taken at a photon energy of 33 eV at various emission angles. The results are shown for two temperatures of 295 K (o) and 235 K (+) for a 30 Å thick film of gadolinium on W(110).

and half width across T_{cs} and T_{cb} we postulate to be a result of short-range magnetic order within the surface layer. This phenomenon will be discussed in greater length in a subsequent paper.

From the quasiparticle spin polarized calculation of Borgiel, Borstel and Nolting [7], we can plot out the total spin-integrated density of states as seen in figure 3. Several assumptions must be made in order to effect a comparison of their calculation with our data because we are attempting to compare a calculation on the total density of states with results from one point in k-space (which are clearly k dependent). From the photon energy and temperature dependence of the bulk bands, we believe that we are observing both bulk bands along Γ to A of the bulk band structure, consistent with other photoemission studies [31, 32]. If we are only observing one of the bulk bands from Γ to A of the bulk band structure then upon analysis of the photoemission spectra, we must invoke a redistribution of oscillator strength between minority and majority spins with temperature. This is most unlikely. By assuming that the flat parts of the band structure contribute the greatest intensity to the integrated density of states and that the 5d bands from Γ to A of the bulk Brillouin zone having the greatest binding energy [33–39] contribute to the features with the greatest binding energy in the integrated density of states, the shift to lower binding energies of

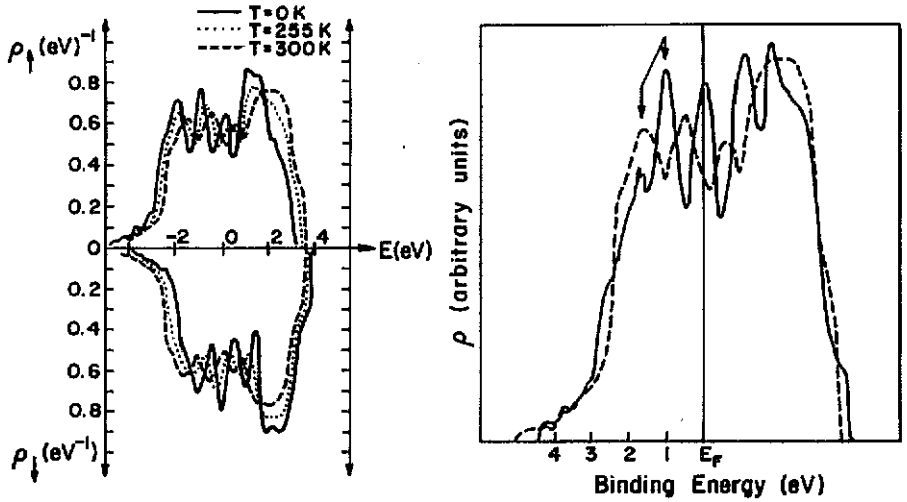

Figure 3. The calculated temperature-dependent density of states by Borgiel *et al* [7] both spin resolved (left) and spin integrated (right). The arrow indicates the temperature-dependent shift of the combined bulk band feature corresponding to the photoemission results of this work.

the bulk bands with decreasing temperature can be qualitatively understood. This binding energy shift of the bulk bands is a result of summing both majority and minority spin states from quasiparticle calculation, as seen in figure 3. We postulate that the two bulk bands that appear in the band structure from Γ to A of the bulk Brillouin zone each have a pair of spin majority and minority components. Each majority spin component shifts in binding energy relative to the minority component with temperature. The sum of all four features leads to a shift to smaller binding energies with decreasing temperature as indicated by our photoemission results and the quasiparticle calculation [7].

Since the combined bulk band photoemission feature not only shifts with temperature but is also accompanied by a change in half width, it is evident that there must exist a temperature dependent exchange splitting, regardless of whether the comparison with the quasiparticle calculation is correct or not. Indeed, we have obtained the first direct experimental demonstration of a temperature dependent band structure in a highly local magnetic moment system.

The amount of the binding energy shift of the bulk bands (0.4 to 0.5 eV) suggests that the exchange splitting of the gadolinium 5d bands changes dramatically from 300 K to 200 K. Such a result is consistent with SPLEED exchange assymmetry results over the same temperature range [8]. On the basis of the quasiparticle calculations of Borgiel *et al* [7] and our results, we believe that the exchange splitting is greater than or equal to 0.9 eV for the ground state. This value is much larger than has been observed for finite temperature (220 K) [40–43], but is consistent with recent calculations for 0 K [19] which predict a bulk 5d exchange splitting of about 0.85 eV.

The results presented here for gadolinium are unlike those obtained for iron [44] which does not exhibit an exchange splitting that depends strongly upon temperature. This is typically interpreted to be a result of the presence of a local magnetic moment and short-range order, even at temperatures above T_c, though for nickel there may also be short-range order for $T > T_c$ [1–4]. In comparison, the fact that the gadolin-

ium band structure changes dramatically as a result of magnetic ordering suggests that short-range order in the bulk is much smaller than for a ferromagnetic systems such as iron, or that the 5d itinerancy is very great and increases the interatomic correlation.

Our results indicate that the exchange splitting is dependent upon the position in k-space, as determined by photon energy, and emission angle (figure 2). Such a k-dependent exchange splitting is similar to results obtained for iron [45, 46]. The k dependence of the exchange splitting could be responsible for the failure of other measurements to observe a temperature dependence of the band structure.

In conclusion, we demonstrated that magnetic order induces a change in the electronic structure of gadolinium. This change appears to be qualitatively in agreement with the quasiparticle calculations [7]. The temperature dependence of the bulk band structure is sensitive to position in k-space and is indicative of a very large 5d exchange splitting at $\overline{\Gamma}$ (possibly larger than 0.9 eV at 0 K for this region along Γ to A of the bulk band structure).

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