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Temperature-dependent electronic structure in a localized-magnetic-moment system: Gadolinium

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At normal emission, the bulklike band in gadolinium overlayers on W(110) shifts toward E_F from 1.64 eV at 310 K to 1.43 eV at 230 K in photoemission. This is accompanied by an increase of the feature width from 0.8 eV at 320 K to 1.1 eV at 230 K. The surface-state binding energy remains unchanged, though the width increases significantly with increasing temperature. The different effects of temperature upon the photoemission results obtained for the bulklike and surface states are interpreted as magnetic-order-induced band movement and spin mixing, respectively, and are discussed in the light of a quasiparticle theory. The band dispersion along $\bar{\Sigma}$ is also temperature dependent. We postulate that the exchange splitting of the conduction band is not uniform at different positions in **k** space.

I. INTRODUCTION

Temperature-dependent band-structure studies in magnetic systems, especially in Fe (Refs. 1-3) and Ni,[4,5] have attracted extensive interest. In part, this interest is motivated by the controversy associated with the theoretical explanation of the temperature-dependent band structure and the existence and extent of local-magnetic-moment and short-range order. For Fe, no significant binding-energy shift in valence-band photoemission spectra is observed with temperature change. For Ni, a decreasing exchange splitting is observed with temperature increase, but the exchange splitting does not drop to zero at T_c.[4] These results challenge the traditional Stoner model[6] for itinerant-electron magnets and lead to various theories such as "local band theory",[7] "disordered-local-moment" theory,[8] and some recent quasiparticle theories.[9] In ferromagnetic 3*d* transition metals, the itinerant conduction electrons both produce magnetic order and display an exchange splitting. In order to understand better the relation between the magnetic order and electronic structure, it is worthwhile to study some local-magnetic-moment-dominated systems, such as the heavy rare earths, for comparison.

In spite of the importance of studying a local-magnetic-moment ferromagnet such as gadolinium, there exist only a few temperature-dependent valence-band studies of rare-earth metals[10,11] because of technical difficulties. For the most part, these investigations found few temperature-dependent changes of electronic structure of gadolinium or the other rare earths. In this study, we provide experimental evidence for the temperature-dependent electronic structure in gadolinium films.

Gadolinium is known not only as a typical local-magnetic-moment system, but also a classical example for unusual surface magnetism. Weller *et al.*[12] and several other groups[13,14] reported that the surface layer exhibits a Curie temperature of 315 K, 22 K higher than the bulk T_c of 293 K, and that the surface couples antiferromagnetically to the bulk. The unusual surface magnetic properties of gadolimium are also consistent with the electronic structure. A highly localized surface state near E_F has been studied experimentally[15,16] and theoretically[17,18] for gadolinium and good agreement is found between theory and experiment. For these reasons it is worthwhile studying the magnetic-order-induced properties in both surface and bulk states in Gd, and thereby obtain insight into the unique surface magnetic properties observed in this particular system.

In this work, we report our study of magnetic-order-induced electronic structure changes in a typical local-magnetic-moment system. We will present the temperature dependence of the valence band of Gd overlayers on W(110). We shall demonstrate that the surface state and bulklike state exhibit different types of temperature-dependent behavior. A simple picture is employed to understand these differences and we indicate that the surface-state electrons are very spatially localized.

II. EXPERIMENT

A gadolinium overlayer on W(110) can adopt the crystal structure of bulk Gd with the (0001) face perpendicular to the surface normal.[12,19,20] This provides an ideal system to study films of exceptional purity.

The gadolinium films used in this study are prepared with well-established methods described in detail elsewhere[19-21] in a vacuum system with a base pressure of $(5-8)\times10^{-11}$ Torr. The W(110) substrate was cleaned by the accepted procedure of heating in O_2 and flashing.[22] Evaporated Gd was deposited onto W(110) substrate at room temperature with the evaporation rate of 1–3 Å/min and the film thickness was monitored with a quartz-crystal oscillator. The pressure during the deposition never exceeded 1×10^{-10} Torr. The error in relative thickness was small ($<2\%$) while the absolute value of the thickness can only be taken as nominal thickness. Impurities and contamination on the substrate and the films were monitored with Auger electron spectroscopy (AES) and photoemission. No trace of C or O was detected within the instrumental limit (1–2 % for AES and even lower for photoemission) on the substrate before the deposition and the films after the photoemission experiment. Low-energy electron-diffraction (LEED) studies were undertaken to confirm that the Gd films were well ordered with the *c* axis parallel to the surface normal, consistent with previous results by other research groups.[19,20] No structural change was observed from 300 to 200 K. To avoid the potential contamination that may alter the surface layer and/or the magnetic properties of the overlayer, all the photoemission data were taken shortly after the deposition.

The temperature of the sample was measured with a *W*-5%*Re*/*W*-26%*Re* thermocouple with an accuracy of 5 degrees Kelvin largely as a result of systematic errors which were the greatest source of temperature uncertainty. The temperature range was 200–510 K.

The angle-resolved photoemission experiments were performed on a system equipped with hemispherical electron-energy analyzer as described elsewhere.[21] The uv light, typically 33 and 40 eV in this study, was dispersed by a 6-m toroidal grating monochromator at the Synchrotron Radiation Center in Stoughton, Wisconsin. The incident light of 37° or 70° off normal was used to provide larger portion of light with its vector potential parallel to or perpendicular to the thin film (*s* or *p* polarization, respectively). The photoelectrons were collected normal to the surface ($\bar{\Gamma}$) or off-normal along a particular high-symmetry direction ($\bar{\Sigma}$ in this study). "Even geometry" was used because of the symmetry of the Gd valence bands.[15,17] The combined (including the monochromator and electron-energy analyzer) photoemission energy resolution was 100 meV for the temperature-dependence experiments. The binding energies in this work are referenced to the Fermi level.

III. IDENTIFICATION OF A GADOLINIUM SURFACE STATE

We have identified the Gd valence-band features in the photoemission energy distribution curves as discussed in preliminary reports elsewhere.[15,16] This is essential for understanding the temperature-dependent effects of the valence-band electronic structure.

Figure 1 shows the gadolinium valence-band spectra of the films with different thickness. The feature at 8.6 eV is well established to be a consequence of the occupied 4*f* states,[21] which is not observed to vary with thickness apart from a surface-to-bulk core-level shift.[23] The part of the spectra near E_F (0–3 eV) changes with the coverage. For very low coverage, only one photoemission feature is readily apparent. With film thicknesses larger than 10–15 Å, two photoemission features appear with one sharp peak just below E_F and another broad feature at 1∼2 eV binding energy. The binding energy of this latter feature changes with thickness. The broad feature exhibited a clear dispersion with changing photon energy, i.e., with change in $k_\perp$. We, therefore, identify this feature as a developing bulklike state. This feature resembles the two states of the bulk Gd at $\bar{\Gamma}$ as observed by Himpsel *et al.*[24] and calculated by Freeman and other researchers.[25] The sharp feature near the Fermi level has only recently been observed, as discussed in our reports.[15,16] This photoemission feature satisfies the three basic criteria[26] for a surface state: First, the binding energy of this state is independent of the incident photon energy, and therefore change in $k_\perp$; thus this state exhibits the two-dimensionality of the state. Second, this state is in a gap of the projected band structure as indicated by bulk band-structure calculations.[17,18,25] Third, this feature is very sensitive to surface contamination. Leaving the film overnight in an 8×10^{-11} Torr vacuum or doping with a small amount of oxygen (less than even 0.1 L) can weaken this state significantly.[16] We therefore identify this state as a surface state on the Gd(0001) surface located principally in the vicinity of $\bar{\Gamma}$.[15]

Figure 2 shows that both the bulklike and the surface states are significantly enhanced under *p*-polarized light

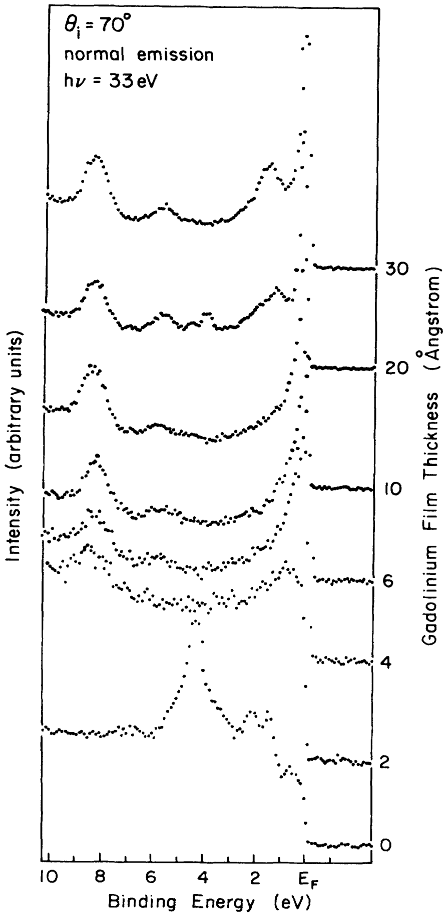

FIG. 1. Photoemission spectra of gadolinium overlayers on W(110). The photoelectrons were collected normal to the surface. The incidence angle of the synchrotron radiation was 70° (*p* polarized) so as to increase the relative signal of the surface state relative to the other bands. The photon energy was 33 eV.

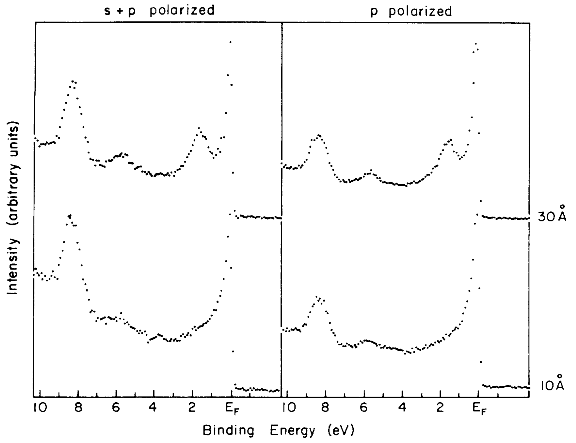

FIG. 2. Photoemission spectra of 10- and 30-Å gadolinium overlayers on W(110). All photoelectrons were collected normal to the surface and the photon energy was 33 eV. The light incidence angles were 70° (p polarized) and 34° ($s+p$ polarized). Both the 5d surface and bulklike states show $5d_{3z^2-r^2}$ character, as indicated in the text.

compared with the 4f state (which should be very isotropic). This indicates both states have mainly $d_{3z^2-r^2}$ character.[15] The symmetry and binding energy of this surface state are found to be in good agreement with the calculated surface state independently predicted by Wu and Freeman.[17,18] They predicted a very localized surface state of $d_{3z^2-r^2}$ character near E_F in the vicinity of $\bar{\Gamma}$ on Gd(0001). The experimental and theoretical band structure along $\bar{\Sigma}$ also shows very similar trends.[15,17] The calculated band structure of the surface state indicates that this state exhibits little dispersion before it hybridizes with the bulk band half way from $\bar{\Gamma}$ to $\bar{M}$, consistent with our experimental results. Wu and Freeman claim that this surface state is a magnetic surface state with its purely polarized spin antiparallel to the majority spins of the bulk. This has yet to be demonstrated directly with spin-polarized photoemission. Nonetheless, we find good agreement between the theory and our experiments, based on the qualitative shape of the band dispersion, and the location and symmetry of the surface state.

IV. TEMPERATURE DEPENDENCE OF THE BULKLIKE AND SURFACE STATES

The spectra of a typical 30-Å Gd film for various temperatures are shown in Fig. 3. Notice that the maximum of the bulklike band shifts to lower binding energy when the temperature is lower than 300 K and the feature become asymmetric at the same time. In Fig. 4, several sets of the bulk binding energy (at the maximum) before background subtraction from several different 30-Å films are superimposed on one another. The scatter of the data points reflects the random and systematic error (mainly caused by the different sets of data) in this experiment. At the low-temperature end, the peak shifts from 1.64±0.07 eV at 310 K to 1.43±0.02 eV at 230 K and

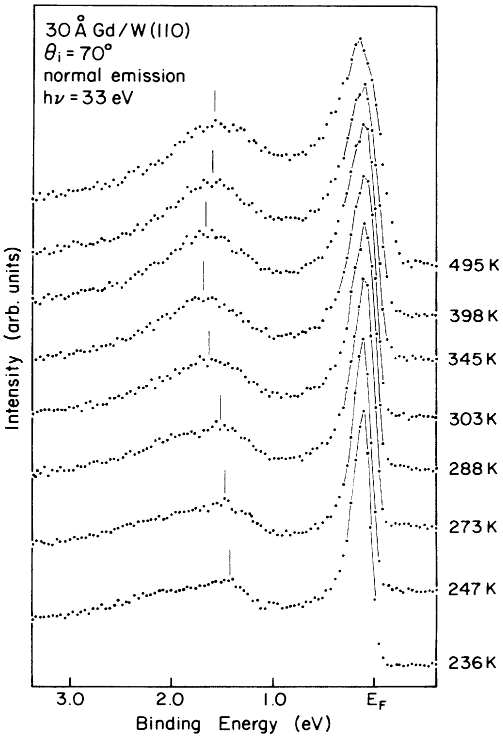

FIG. 3. The temperature dependence of the photoemission spectra of a 30-Å Gd film on W(110). Photoelectrons were collected at normal emission ($\bar{\Gamma}$) and the light incidence angle was 70° off the surface normal (p polarized). The shift in the bulk bands is indicated. The photon energy was 33 eV.

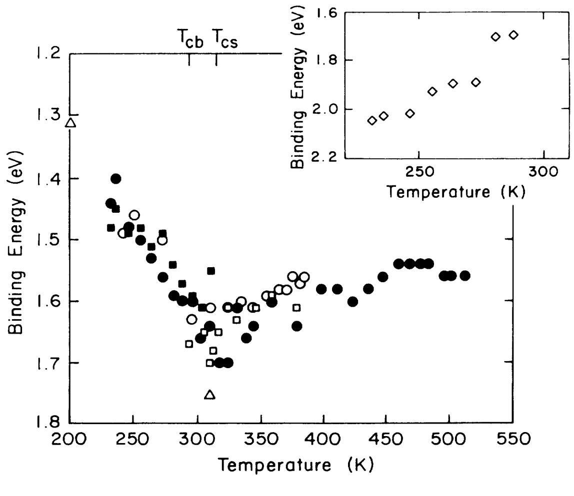

FIG. 4. The temperature-induced binding-energy shift of the bulklike feature of Gd films derived from the spectra in Fig. 3 and other similar spectra of several different 30-Å films. Different symbols represent different sets of data. The inset shows the temperature dependence of one component of the bulklike feature. This may be qualitatively representative of the Δ_1 majority-spin state temperature dependence as discussed in the text.

1.3 eV at 200 K. At the high-temperature end, a reproducible shift away from E_F of about 100 meV is observed as the temperature is lowered from 510 to 310 K. These shifts are reversible with repeated temperature cycles within experimental error. The maximum binding energy is observed around 310 K. Subtracting the background does not change the basic trends of the bulk band binding-energy shift, though the absolute values themselves can alter slightly.

The inset of Fig. 4 shows the binding energy of a small component ($\sim 20\%$ of the total intensity) obtained by trying to fit the bulk state with two Lorentzian functions. This component reflects the trends of the bulk feature splitting apart and therefore becoming asymmetric, though the absolute value of the shift is not necessarily representative of the true change of the component with temperature because the fitting is not unique.

Figure 5 summarizes the temperature dependence of the linewidth of the same bulklike feature at 1–2-eV binding energy seen in Fig. 3. It is clear that, accompanying with the binding-energy shift at the lower temperatures, the linewidth increases from 0.8 eV at around 320 K to 1.1 eV at around 230 K. For $T > 320$ K, no sizable width change of the bulklike feature with temperature is observed with our present signal-to-noise ratio, and within the limitations presented by the scatter of our data.

From Fig. 3, it is apparent that the width of the surface state becomes narrower in energy with decreasing temperature. The binding energy remains fixed within experimental error for the surface state observed for the thicker films. Figure 6 shows that the width of the surface state decreases nearly linearly from 0.55 eV at 510 K to 0.22 eV at 230 K. We have not identified any abrupt change in this feature with temperature across T_c.

The band structure along $\bar{\Sigma}$ (from $\bar{\Gamma}$ to $\bar{M}$) is measured at room temperature and 230 K by collecting the off-normal photoelectrons at different emission angles, i.e., different $k_{\parallel}$. The binding energy vs $k_{\parallel}$ is plotted out in Fig. 7. It is obvious that the shift due to the temperature change is not uniform at the different places in the k space and the bands at different temperature cross over at about half-way from $\bar{\Gamma}$ to $\bar{M}$.

It is also observed that, for the different photon energies, i.e., different $k_{\perp}$, the temperature-induced binding-energy shift of the bulklike state is different. This could be one of the reasons that this temperature dependence was not observed by other experimentalists.[10,11] The results for both $k_{\parallel}$ and $k_{\perp}$ dependence together show clearly that the temperature dependence of the band structure is sensitive to position in the Brillouin zone.

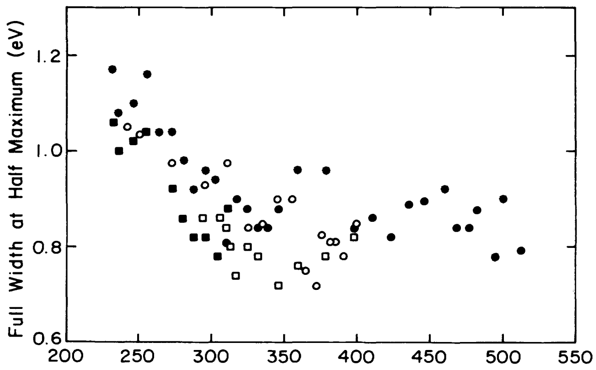

FIG. 5. The temperature dependence of the linewidth of the bulklike feature derived from Fig. 3 and other similar spectra. The different symbols represent different sets of data from several different 30-Å Gd films.

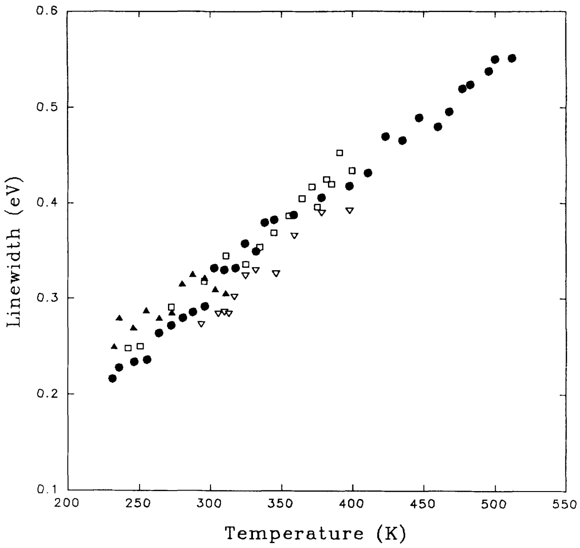

FIG. 6. The surface-state linewidth change with temperature derived from Fig. 3 and other similar spectra for different 30-Å Gd films. The different symbols represent different sets of data.

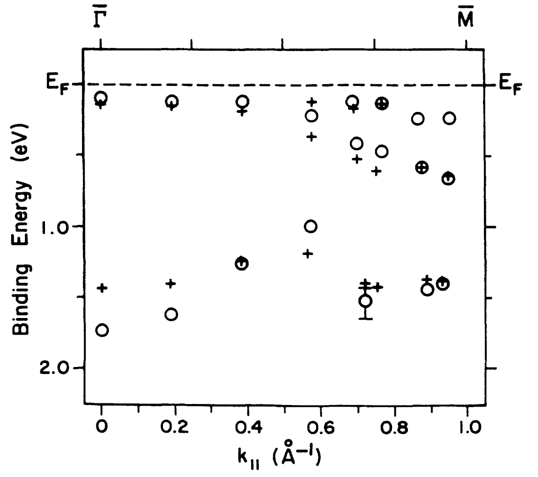

FIG. 7. The experimental band structure from $\bar{\Gamma}$ to $\bar{M}$ of the surface Brillouin zone from spectra taken at a photon energy of 33 eV at various emission angles. The results are shown for the two temperatures of 295 K (o) and 235 K (+). The results are for a 20-Å film of gadolinium on W(110).

V. TEMPERATURE DEPENDENCE OF THE ELECTRONIC STRUCTURE IN THE THINNER FILMS

As shown previously, for the films thinner than 10 Å, the valence-band spectra are dominated by one feature near E_F (Fig. 1). Figure 8 illustrates the temperature dependence of the valence band of a 5-Å film. At low temperature, the position and shape of the feature near E_F are very similar to that of the surface state in thicker films (≥ 30 Å). In contrast to the surface state in thicker films, however, the binding energy of the feature near E_F shows an observable shift toward higher binding energy with increasing temperature as summarized in Fig. 9 for a 5-Å film. Instead of the apparent linear dependence of the linewidth observed for the thicker films over the whole temperature range, the thinner films are seen to have a linewidth of this state near E_F which remains constant for temperatures higher than 340 K, though still showing a decrease from 0.72 eV at 340 K to 0.25 eV at 236 K as seen in Fig. 10.

There are also profound differences between the normalized intensities of the state observed near E_F in the thinner films and the intensity of the surface state observed for thicker films as seen in Fig. 11. The intensity of the surface state for the thicker films remains virtually constant with temperature, while for the thinner film, the

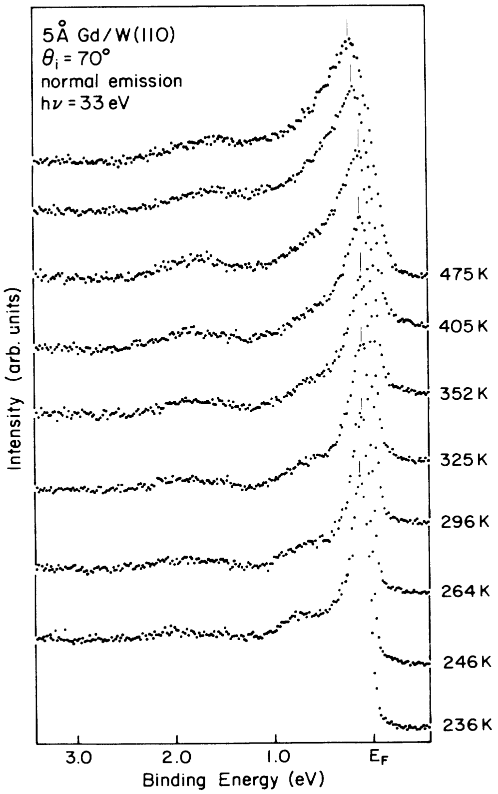

FIG. 8. Photoemission spectra of a 5-Å Gd overlayer on W(110). Photoelectrons were collected at normal emission under *p*-polarized light of 33 eV. The shift of the prominent feature is indicated.

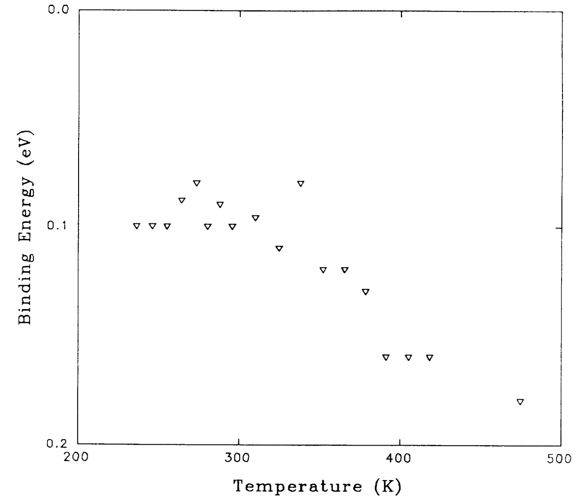

FIG. 9. The temperature dependence of the binding energy of the prominent feature in a 5-Å thick Gd film, derived from Fig. 8.

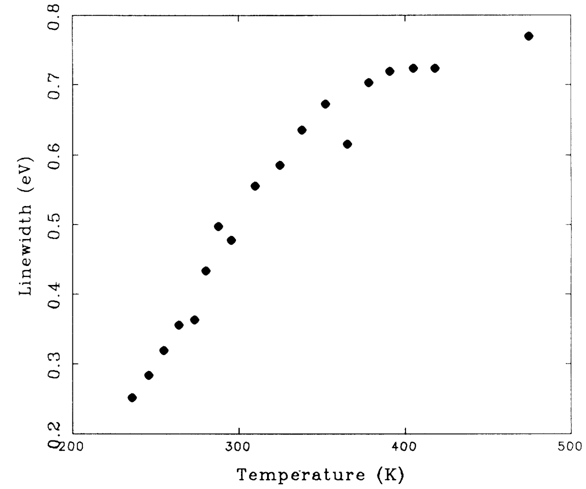

FIG. 10. The temperature dependence of the linewidth of the prominent feature in Fig. 8.

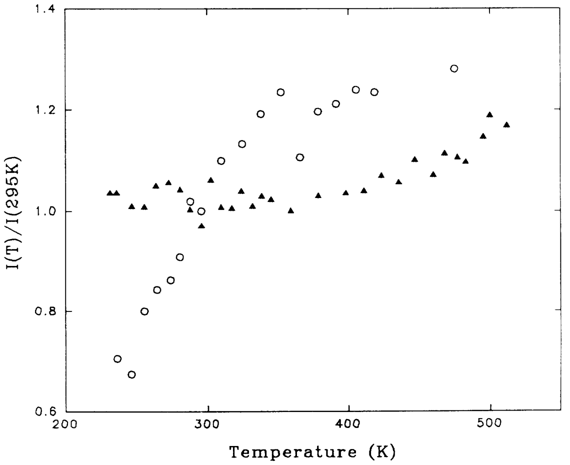

FIG. 11. The temperature dependence of the intensities of the prominent feature in 5-Å film (○) and the surface state for a 30-Å film.

intensity is only constant above 350 K and decreases upon cooling below 350 K.

In Fig. 8, a weak feature of about 0.8 eV is resolved at 230 K. With increasing temperature, this feature becomes difficult to resolve, finally disappearing in the strong feature near E_F, which (as indicated above) has a dramatic increasing width with increasing temperature. The binding energy of this feature at about 0.8-eV binding energy cannot be reconciled with any bulk Gd or W(110) band-structure features.

VI. DISCUSSION

A. Elimination of several temperature-dependent effects

Before we try to interpret our experimental results, several other temperature-dependent effects can be eliminated as the origin of our observed temperature effects. Temperature-dependent changes are observed for rare-earth metals such as cerium,[27] but such changes are typically abrupt and can be associated with structural phase transitions. In this study, major structural phase transition and contamination can be ruled out immediately by LEED. Contamination can also be eliminated since Auger electron spectroscopy and photoemission measurements did not exhibit any difference before and after the experiments. The temperature-dependent effects observed in photoemission were also reproducible with temperature cycles.

For $T\neq 0$ K, a Fermi distribution will contribute to the spectra and especially alter the shape of Fermi edge with temperature. This will cause some broadening of any feature next to E_F like the surface state in Gd. This broadening, however, should be at the order of $k_BT\sim 0.025$ eV. So the Fermi distribution should not have a noticeable contribution to the measured linewidth of the surface state in our experiment.

Several temperature-dependent effects in photoemission (other than structural phase transition) have been previously studied.[28–31] Since phonon distribution changes with temperature, phonon-related effects such as phonon-assisted indirect transition and phonon broadening will result in temperature-dependent photoemission spectra.

Considering that the indirect transition ($\Delta\mathbf{k}\neq\mathbf{0}$) can be assisted by the phonon with proper wavelength, the intensity of the photoemission features should decrease with increasing temperature as investigated theoretically[28] and experimentally.[29] The temperature-dependent cross section is[28,29]

$$\sigma_{\text{tot}}=e^{-CT}\sigma_1+(1-e^{-CT})\sigma_2\ , \tag{1}$$

where $C=|\Delta\mathbf{k}|^2(3\hbar^2)/(Mk_B\Theta_D^2)$, Θ_D is the Debye temperature of the material, $\Delta\mathbf{k}=\mathbf{k}_f-\mathbf{k}_i$, and σ_1 and σ_2 are direct and indirect cross sections, respectively. Noting that σ_2 is small for ultraviolet photoemission and the bulk Gd Debye temperature is about 185 K,[32] the intensity change $\Delta I/I$ in our temperature range should be as small as 3%. This is smaller than our experimental error (estimated as 5% for the surface state and larger for the bulklike state). In fact, as shown in Fig. 10, the intensity of the surface state does not show a decrease with increasing temperature as would be expected for pronounced phonon interactions. So the phonon-assisted indirect transition picture is not applicable in explaining our observations.

Another temperature-dependent effect is phonon broadening resulting from phonon excitation during the photoemission process.[30] In the Debye solids, the linewidth caused by this effect should change with temperature as

$$\Gamma_{\text{el-ph}}=\frac{C}{\Theta_D^{1/2}}\left[1+\left[\frac{8T}{3\Theta_D}\right]^2\right]^{1/4}\ , \tag{2}$$

where Θ_D is the Debye temperature. This is not consistent with our surface-state linewidth data since it predicts a much smaller linewidth change (about 0.13 eV at most from 510 to 230 K) than the experimental data (about 0.33 eV in the same temperature range). Furthermore, the functional form of Eq. (2) is difficult to reconcile with the experimental data. For the bulklike state, the experimental linewidth decreases with increasing temperature, instead of increasing as predicted. So, the phonon-broadening effect cannot effectively explain our experimental results.

Temperature related lattice constant changes (for example, thermal expansion) can cause binding-energy shifts because of the changing bonding length and the change in the absolute E_F.[30,31] However, these effects are typically very small, and result in energy shifts of much less than 0.1 eV. This cannot account for the big binding-energy shift of the bulklike state observed below room temperature.

Furthermore, for the bulklike state, the temperature dependence is clearly strongly influenced by position in **k** space and thickness. This is difficult to reconcile with any explanation other than changes in the electronic band structure as a result of magnetic ordering.

B. Temperature-dependent exchange splitting of the bulklike state

The obvious binding-energy shift and the linewidth change of the bulklike feature at $T<310$ K are consistent with the picture that the exchange splitting between the majority- and the minority-spin states changes with temperature in ferromagnetic gadolimium. From photoemission studies, the similar magnetic-order-induced band movement have been observed in Ni (Refs. 4 and 5) by other investigators though the complexities exist. In general, the exchange splitting is expected to decrease with increasing temperature consistent with the magnetization $|\mathbf{M}|$ decreasing. This is a well-known magnetic-order-induced effect in electronic structure. For the case in which the majority and minority features are not well resolved, a decrease in the exchange splitting will result in a narrowing of the linewidth, consistent with our experimental observation on the bulk state width with increasing temperature.

The binding-energy shift and the asymmetric shape at low temperature also indicate that the features shift with respect to each other with temperature change. The attempt of fitting that feature with two Lorentzian functions as seen in Fig. 4 suggests that the features are moving toward each other with temperature increasing. In the exchange-splitting collapsing picture, the two moving features should be the majority- and minority-spin components of the same band. Therefore, for the features well away from E_F (then both components are occupied), the intensity of the two features should be the same. Since the intensities of the two features are totally different ($\sim$1:4), this two-component picture (single band on $\bar{\Sigma}$) is not realistic. Bulk band-structure studies[24,25] also indicate that there are two, not one, bulk bands along $\bar{\Sigma}$. Our bulklike feature appears to qualitatively resemble the bulk band structure of Gd. It may be more realistic to assume that the bulklike feature is composed by four subfeatures split (by exchange splitting) from two features. By using four Lorentzian functions and keeping the intensity of each pair of peaks equal, we can simulate the temperature dependence of the both binding-energy shift and the width change as observed in the experiments. However, since the way of choosing the parameters of the four peaks is not unique, the only conclusion we can draw from this is that the four-component picture is consistent with our experimental results.

The component of the bulk band structure shown in the inset of Fig. 4 can be taken representative of the behavior of the Δ_1 spin majority component of the bulk band structure. This is based upon the asymmetric lineshape analysis and inspection of the bulk band structure[25] and is supported by the experimental band structure of Himpsel and Reihl.[24]

C. Spin mixing in the surface state

The data indicate that the exchange-splitting change picture is not valid in describing the surface state in the thicker films. In contrast to the bulk band feature, the binding energy of the surface state shows little shift with temperature. Although the linewidth increases linearly with temperature increasing, the intensity does not change much. For the features next to E_F, as describes the surface state, the intensity should scale with the width in the exchange-splitting change picture since some states should move across the E_F at $\bar{\Gamma}$. The failure of the exchange-splitting collapse scheme is abundantly clear from a comparison of Figs. 6 and 10, and Fig. 11.

The results obtained for the Gd surface state on thicker films are similar to the behavior seen for Fe,[1] where the binding energies also stay nearly stationary in energy. Nolting[33,34] proposed that, for some rare-earth compounds, with increasing temperature, the exchange splitting will not change much with temperature. Rather the minority (majority) spins start appearing around the majority (minority) spins, i.e., spin mixing. With this picture we can understand the relatively stationary binding energy and the increasing linewidth accompanying the change of the local magnetization.

Notice that the surface-state width keeps increasing for temperatures higher than the surface Curie temperature T_{cs} (Fig. 6). If the origin of the surface-state width change is from the magnetic order (as we proposed in this study), then this result suggests that there is changing short-range order above the surface Curie temperature. This short-range order causes the spin subbands to keep changing with temperature for $T > T_{cs}$. The bulklike state also exhibits a slight binding-energy shift for $T \geq T_{cb}$. This may also indicate the existence of the short-range order in the bulk. For $T/T_c = 1.2$, application of mean-field theory to surface studies of gadolinium thin films does provide evidence that the correlation length, while small (about 3 Å) is not zero.[35,36] Child[37] investigated the magnetic short-range order in Gd with a quasielastic neutron-scattering technique and claimed that there is short-range order, mainly in the basal plane of the bulk Gd, both below T_c (150 K $< T < T_c$) and above T_c. The short-range order for $T > T_c$ decayed very slowly to a temperature as high as around 400 K.[37] Our result is basically consistent with the results of Child[37] although the results for the surface state indicate short-range order persists to even higher temperatures ($\sim$510 K) than is observed by Child. Child's work is a study of the bulk because of the use of the neutron-scattering technique. We should mention that the temperature dependence of the electronic structure can be sensitive to the short-range order since there is not the usual relative spin orientation limitation as is the case for most conventional magnetic measurements.

For the thinner films (with only one prominent valence-band feature at $\bar{\Gamma}$), although the shape and the binding energy of the feature near the Fermi level are very similar to those of the surface state for thicker films (Fig. 8), its behavior with temperature change is significantly different. Instead of remaining almost constant, the normalized intensity increases linearly with increasing temperature for $T < 350$ K and remains virtually constant for $T > 400$ K (as seen in Fig. 11). This intensity behavior almost exactly follows the temperature-dependence curve of the linewidth for this feature near E_F (Fig. 10).

The photoemission feature at 0.8 eV at 230 K (for the thinner films) appears to shift in binding energy toward E_F with increasing temperature. The origin of this state at 0.8-eV binding energy has not yet been identified. One possibility is that this feature is a Gd/W(110) interface state since it belongs to neither W(110) nor Gd. Interface states are not unknown for thin metal overlayers and often have substantial oscillator strength.[38,39]

Assuming the effect of the weak feature at 0.8 eV in the thinner film can be neglected, the temperature dependence of the intensity, linewidth, and binding energy of the prominent feature (Figs. 9–11) suggests that the influence of magnetic order for this state is unlike that observed for the surface state in the thicker films. The data is consistent with additional bands dropping below E_F at $\bar{\Gamma}$ with increasing temperature. Instead of spin mixing, it is more likely that the bands move with temperature change, i.e., exchange-splitting collapse. This indicates strong differences in the itinerancy of this state as compared with the itinerancy of the surface state in the context of the picture discussed below.

The thinner films exhibit a temperature-dependent electronic structure which does not change substantially for temperatures above 400 K. For the thicker films, dramatic temperature-dependent changes are observed for temperatures well above 400 K. Assuming that the electronic structure of the thinner films is mainly affected by the states dropping below E_F at $\overline{\Gamma}$ with increasing temperature, then the results suggest short-range order coupling is weaker in the thinner films for $T > T_c$. This is also consistent with the lower T_c of 271 K (Ref. 14) (as opposed to $T_{cs} = 315$ K and $T_{cb} = 293$ K observed for thick films) observed for monolayer films.

D. Itinerancy and the different type of temperature-dependent effects

The exchange splitting of $5d,6s$ electrons is believed to be caused by the intra-atom exchange interaction between $5d,6s$ and $4f$ electrons. So the temperature-dependent electronic structure should reflect one or both of the changes of magnetic order and of the interaction. We propose a simple picture to qualitatively understand the different behavior of the magnetic electronic states. This understanding is based upon the itinerancy of $5d,6s$ electrons. Basically, an exchange splitting should exist for the states with unpaired spins when a nonzero effective magnetic moment is present because of exchange interaction. If one electron in a particular state is localized within the range of one atomic distance, then this state should always show the maximum exchange splitting because of the large local magnetic moment. The exchange splitting is relatively independent of the kind of magnetic state, though the direction of individual spin may vary with the change in magnetization. In contrast, if the itinerancy of the conduction electrons is very large, then a large number of local magnetic moments in different atoms interact with one $5d,6s$ electron. The exchange splitting of this itinerant $5d,6s$ state should be very sensitive to the change on the relative orientation of the local spins and therefore the long-range magnetization. The key factor for the two kinds of temperature-dependent behaviors is the competition of the itinerancy and the magnetic correlation length. A clear exchange-splitting collapsing indicates the itinerancy of the $5d,6s$ electronic state is large or the correlation length of the $4f$ magnetic moment is small. Spin mixing indicates a relatively more localized state or a very large magnetic correlation length. This picture is undoubtedly oversimplified, but we believe it describes the physical basis of the various temperature-dependent behaviors upon the electronic structure.

We believe that our qualitative argument on the relationship between itinerancy and the temperature dependence of the electronic structure is included in the quasiparticle calculations of Nolting and co-workers.[33,34] In their work, the zero-bandwidth limit (i.e., atomic limit) leads to four distinct quasiparticle levels with temperature-dependent distribution among them, which can be considered as a pure spin-mixing limit in the langauge of this paper. With finite bandwidth (a nonzero itinerancy), the quasiparticle features change shape and shift in energy with temperature. This shift reflects the transition between the spin mixing and exchange-splitting collapsing controlled by bandwidth (i.e., itinerancy). This theoretical picture is consistent with our simple picture.

The exchange-splitting collapse and spin mixing have been previously observed in different materials. In the present study of Gd, both effects are observed for different states. Based on either our simple picture or the ideas presented in the work of Nolting and co-workers,[33,34] our results suggest that the electrons of the surface state for thicker films are more localized than those of the bulklike state. This is consistent with the fact that the surface state shows little dispersion along $\overline{\Sigma}$ before hybridizing with the bulk bands. This absence of dispersion indicates less itinerancy along the relative direction in real space.[15] Wu and Freeman's calculation also indicates a very localized surface state. One of their results is that the Gd(0001) surface expands outward (for about 6.3%).[17,18] The lattice expansion favors localization at least along the surface normal direction.

To our knowledge, there are no published theoretical calculations that predict these effects, though we were recently informed that some temperature-dependent Gd band-structure calculations are underway.[40] The suggestion has been made[41] that the exchange interaction in Gd changes with temperature. This can only be well understood after understanding the temperature dependence of the $5d$-$4f$ interaction, band structure, and the $5d,6s$ electron distribution. As a typical local-magnetic-moment system, the relation between the magnetic order and the electronic structure is not yet fully understood.

E. Anisotropy of the exchange splitting

The band structures along $\overline{\Sigma}$ in Fig. 7 show that the temperature-induced binding-energy shift is not constant at different places in **k** space. Since this temperature-induced shift is an indication of the exchange-splitting change, our result suggests that the exchange splitting is not uniform in reciprocal space. Similar effects were observed in Fe (Ref. 42) and some other materials. However, a detailed comparison with theory is necessary to obtain more insight into this effect.

An alternative way to explain our experimental results is to consider the particular shape of the Gd band structure. The dependence of temperature-dependent bulk band shift upon $k_{\parallel}$ is qualitatively consistent with the band structure of Wu and Freeman.[17] With increasing $k_{\parallel}$, additional bands contribute to the bulk band structure, dispersing to greater binding energy toward $\overline{M}$.

For $T > T_{cb}$, the shift of the bulk band feature to smaller binding energy may be attributed to a different short-range-order-induced exchange splitting of the Δ_1 bulk bands as opposed to the Δ_2 bands. Thus, different bands may exhibit different exchange splitting, at least for $T > T_c$.

VII. CONCLUSION

In this work, we have demonstrated that there is a surface state on Gd(0001) at $\bar{\Gamma}$, which is very close to the Fermi level and has $5d_{3z^2-r^2}$ character. The valence band develops with increasing thickness: only one prominent 5*d* feature near E_F for the films thinner than 10 Å and two features (one surface state and one bulklike state) for the thicker films (≥ 30 Å). These different 5*d* states show different temperature dependence of the binding energy, linewidth, and intensity, which suggests the exchange-splitting collapse for the bulklike state of the thicker films and the surface state of the thinner films, and spin mixing in the surface state of the thicker films. Our results give some insights into the relation between these two types of magnetic-order-induced electronic-structure behavior at finite temperature.

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[1] E. Kisker, K. Schröder, M. Campagna, and W. Gudat, Phys. Rev. Lett. **52**, 2285 (1984).

[2] R. Clauberg, H. Hopster, and R. Raue, Phys. Rev. B **29**, 4395 (1984); M. Campagna, Physica B + C **127**, 117 (1985).

[3] J. Kirschner, M. Göbl, V. Dose, and H. Scheidt, Phys. Rev. Lett. **53**, 612 (1984).

[4] R. Raue, H. Hopster, and R. Clanberg, Phys. Rev. Lett. **50**, 1623 (1983); H. Hopster, R. Raue, G. Güntherodt, E. Kisker, R. Clauberg, and M. Campagna, *ibid.* **51**, 829 (1983); R. Raue, H. Hopster, and R. Clauberg, Z. Phys. B **54**, 121 (1984).

[5] J. Unguris, A. Seiler, R. J. Celotta, D. T. Pierce, P. D. Johnson, and N. V. Smith, Phys. Rev. Lett. **49**, 1047 (1982); L. E. Klebanoff, R. K. Jones, D. T. Pierce, and R. J. Celotta, Phys. Rev. B **36**, 7849 (1987); M. Donath and V. Dose, Europhys. Lett. **9**, 821 (1989).

[6] E. C. Stoner, Proc. R. Soc. London, Ser. A **154**, 656 (1936).

[7] V. Korenman, J. L. Murray, and R. E. Prenge, Phys. Rev. B **16**, 4032 (1977); **16**, 4048 (1977); **16**, 4058 (1977); H. Capellmann, Z. Phys. B **34**, 29 (1979).

[8] J. Staunton, B. L. Gyorffy, A. J. Pindor, G. M. Stocks, and H. Winter, J. Magn. Magn. Mater. **45**, 15 (1984); A. J. Prindor, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F **13**, 979 (1983); H. Hasegawa, J. Phys. Soc. Jpn. **46**, 1504 (1979).

[9] W. Nolting, W. Borgiel, V. Dose, and Th. Fauster, Phys. Rev. B **40**, 5015 (1989); W. Nolting, J. Braun, G. Borstel, and W. Borgiel, Phys. Scr. **41**, 601 (1990); W. Nolting, S. Bei der Kellen, and G. Borstel, Phys. Rev. B **43**, 1117 (1991).

[10] A. Cerri, D. Mauri, and M. Landolt, Phys. Rev. B **27**, 6526 (1983).

[11] R. G. Jordan, Phys. Scr. T **13**, 22 (1986); G. J. Lapeyre, Phys. Rev. **179**, 623 (1969); A. J. Blogett, Jr., W. E. Spicer, and A. Y.-C. Yu, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris 1965* (North-Holland, Amsterdam, 1966), pp. 246–256.

[12] D. Weller, S. F. Alvarado, W. Gudat, K. Schröder, and M. Campagna, Phys. Rev. Lett. **54**, 1555 (1985); D. Weller and S. F. Alvarado, Phys. Rev. B **37**, 9911 (1988).

[13] C. Rau and M. Robert, Phys. Rev. Lett. **58**, 2714 (1987); C. Rau and S. Eichner, Phys. Rev. B **34**, 6347 (1986).

[14] M. Farle and K. Baberschke, Phys. Rev. Lett. **58**, 511 (1987).

[15] Dongqi Li, C. W. Hutchings, P. A. Dowben, C. Hwang, R. T. Wu, M. Onellion, A. B. Andrews, and J. L. Erskine, J. Magn. Magn. Mater. **99**, 85 (1991).

[16] Dongqi Li, C. W. Hutchings, P. A. Dowben, C. Hwang, R. T. Wu, M. Onellion, A. B. Andrews, and J. L. Erskine, J. Appl. Phys. **70**, 6062 (1991).

[17] Ruqian Wu and A. J. Freeman, J. Magn. Magn. Mater. **99**, 81 (1991).

[18] Ruqian Wu, Chun Li, A. J. Freeman, and C. L. Fu, Phys. Rev. B **44**, 9400 (1991).

[19] J. Kolaczkiewicz and E. Bauer, Surf. Sci. **175**, 487 (1986).

[20] D. Weller and S. F. Alvarado, J. Appl. Phys. **59**, 2908 (1986).

[21] P. A. Dowben, D. LaGraffe, and M. Onellion, J. Phys.: Condens. Matter **1**, 6571 (1989).

[22] R. G. Musket, W. McLean, C. A. Colmenowes, D. M. Makowiezcki, and W. J. Siekhaus, Appl. Surf. Sci. **10**, 143 (1982).

[23] D. LaGraffe, P. A. Dowben, and M. Onellion, Phys. Rev. B **40**, 3348 (1989); D. LaGraffe, P. A. Dowben, and M. Onellion, J. Vac. Sci. Technol. A **8**, 2738 (1990).

[24] F. J. Himspel and B. Reihl, Phys. Rev. B **28**, 574 (1983).

[25] For example, J. P. Dimmock and A. J. Freeman, Phys. Rev. Lett. **13**, 750 (1964); B. N. Harmon and A. J. Freeman, Phys. Rev. B **10**, 1979 (1974); B. N. Harmon, J. Phys. (Paris) Colloq. **40**, C5-65, (1979); W. M. Temmerman and P. A. Sterne, J. Phys.: Condens. Matter **2**, 5529 (1990); J. Sticht and J. Kuber, Solid State Commun. **53**, 529 (1985); T. C. Laung, X. W. Wang, and B. N. Harmon, Physica B **149**, 131 (1988).

[26] E. W. Plummer and W. Eberhardt, Phys. Rev. B **20**, 1444 (1979).

[27] C. Gu, X. Wu, C. G. Olson, and D. W. Lynch, Phys. Rev. Lett. **67**, 1622 (1991).

[28] N. J. Shevchik, Phys. Rev. B **16**, 3428 (1977).

[29] For example, R. S. Williams, P. S. Wehner, J. Stöhr, and D. A. Shirley, Phys. Rev. Lett. **39**, 302 (1977); Z. Hussain, C. S. Fadley, S. Kono, and L. F. Wagner, Phys. Rev. B **22**, 3750 (1980); B. P. Tonner, H. Li. M. J. Robrecht, Y. C. Chou, Marshall Onellion, and J. L. Erskine, Phys. Rev. B **34**, 4386 (1986).

[30] P. H. Citrin and G. K. Wertheim, Phys. Rev. B **16**, 4256 (1977); D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **67**, 116 (1991).

[31] Kevin J. Malloy and James A. Van Vechten, J. Vac. Sci. Technol. B **9**, 2212 (1991), and references therein.

[32] *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneider, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1.

[33] W. Nolting, Phys. Rev. B **32**, 403 (1985).

[34] W. Nolting, W. Borgiel, and G. Borstel, Phys. Rev. B **35**, 7025 (1987).

[35] M. Taborelli, R. Allenspach, G. Boffa, and M. Landolt, Phys. Rev. Lett. **56**, 2869 (1986).

[36] P. A. Dowben, D. LaGraffe, Dongqi Li, G. Vidali, L. Zhang, D. Dottl, and M. Onellion, Phys. Rev. B **43**, 10 677 (1991).

[37] H. R. Child, Phys. Rev. B **18**, 1247 (1978).

[38] J. E. Houston, C. H. F. Peden, P. J. Feibelman, and D. R. Hamann, Phys. Rev. Lett. **56**, 375 (1986).

[39] P. A. Dowben, Y. J. Kime, S. Varma, M. Onellion, and J. L. Erskine, Phys. Rev. B **36**, 2519 (1987).

[40] W. Nolting *et al.* (private communication).

[41] D. R. Westhead, A. Cuccoli, S. W. Lovesey, and V. Tognetti, J. Phys.: Condens. Matter **3**, 5235 (1991).

[42] A. M. Turner and J. L. Erskine, Phys. Rev. B **28**, 5628 (1983); M. F. Onellion, C. L. Fu, M. A. Thompson, J. L. Erskine, and A. J. Freeman, *ibid.* **33**, 7322 (1986).