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Strain-induced distortion of the bulk bands of gadolinium

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Thin films of gadolinium, approximately 8 ML thick, have been grown on the corrugated (112) surface of molybdenum and the electronic structure has been investigated with angle-resolved photoelectron spectroscopy. The unfavorable lattice match between the ''steplike'' Mo(112) substrate and the preferred hexagonally ordered Gd film results in an incommensurate Gd structure that appears to be ordered, but strained along the direction of the corrugations. The hexagonal Gd lattice is expanded by more than 20% along the ''step'' lines of the substrate, as determined from the reduced Brillouin-zone size along the $\overline{\Gamma\Sigma M}$ high-symmetry line and low-energy electron diffraction. The induced strain substantially alters the conventional Gd $5d/6s$ bulk bands to exhibit a dispersion opposite to that of the relaxed Gd(0001) structure. Dislocations destroy the long-range crystallographic order in the direction orthogonal to the corrugations, which results in the localization of the bands along the $\overline{\Gamma TK}$ symmetry line. [S0163-1829(96)00848-X]

The modification of crystalline films of $3d$ transition metals in terms of lattice expansions, or contractions, can significantly alter the electronic structure.[1,2] Some calculations exist for the strained electronic structure of the rare earths [in particular, of Pr (Ref. 3)]. Nonetheless, only a few experimental studies have been performed as a result of the considerable difficulties in preparing strained, crystalline films.[4,5] Small amounts of strain are obtained for ultrathin films of Gd(0001) grown on W(110),[6] but only few differences were observed in the electronic structure which could be attributed to strain.[4]

The experimental band structure of hexagonal closed-packed Gd has been studied extensively.[4,5,7–12] The bulk band structure resembles Stoner-like behavior,[8,13,14] while the surface exhibits a temperature-dependent electronic structure similar to a rigid-band system.[14] The valence- and/or conduction-band electrons are itinerant and are believed to mediate the magnetic exchange coupling of the large local moments of the half-filled $4f$ core levels ($4f^7 5d^1 6s^2$).[15] The magnetic coupling to the nearby atoms is established by partial polarization of the $5d/6s$ valence and/or conduction electrons (indirect coupling). Strain is certainly expected to alter the band structure of the valence and conduction electrons, which will consequently have pronounced effects on the magnetic properties. The effect of strain on the electronic structure of Gd is therefore of fundamental interest. In this paper we will discuss the modified valence-band electronic structure of strained thin Gd films (8–10 ML), which were obtained by growing Gd on a corrugated Mo(112) substrate (with the atomic distance perpendicular to the Mo furrow direction of 4.45 Å). The experimental band structure was mapped using angle resolved ultraviolet photoemission spectroscopy and the structural analysis was undertaken with low-energy electron diffraction (LEED).

The photoemission experiments were carried out in a UHV chamber equipped with a hemispherical electron energy analyzer with an angular acceptance of $\pm 1°$.[16] The light was dispersed with a 6-m toroidal grating monochromator at the Synchrotron Radiation Center in Stoughton, Wisconsin. The combined energy resolution was ~150 meV. The sample temperature was monitored with a Re/W 5–26 % thermocouple with an accuracy of ± 5 K. All photoemission spectra shown in this paper have been acquired at $T \approx 150$ K with a photon energy of 35 eV at an incident angle of 45°.

Thin Gd films of 20–25 Å were grown at approximately 150 K on a Mo(112) crystal by slow thermal deposition. The chamber pressure during deposition was less than 1.5×10^{-10} Torr, while the base pressure was in the 9×10^{-11} Torr range. The Gd film thickness was monitored with a quartz-crystal oscillator that was calibrated by monitoring the attenuation of the molybdenum $4p$ core-level signal and the increased signal of the Gd $4f$ core levels. The as grown films were subsequently annealed at approximately 500 K for 5 min to maximize structural order, as indicated by the development of the bulk band dispersion and LEED.

Low-temperature annealing ($T<500$ K) of the as-deposited Gd films gives an imperfect (1×1) LEED pattern [Fig. 1(b)]. The well-ordered Gd films grown on Mo(112) exhibit a streaked hexagonal LEED pattern, where the streaks are oriented perpendicular to the substrate ''step'' lines [Fig. 1(a)]. This indicates that the Gd films order in a hexagonal structure along the corrugation lines. The streaks imply that misfit dislocations form perpendicular to the ''step'' direction and propagate to the surface of the 8–10-ML-thick Gd films. The ordering of the Gd films is associated with a narrowing of the surface state linewidth, as well as the formation of the Gd $5d/6s$ bulk bands.

Both the strain and the misfit dislocations within the thin Gd films with hexagonal order are manifest in the band dispersion of the $5d/6s$ bulk bands. Figure 2 shows two sets of valence-band photoemission spectra that were acquired for various points along the high-symmetry lines $\overline{\Gamma\Sigma M}$ (top) and $\overline{\Gamma TK}$ (bottom) of the surface Brillouin zone of the strained Gd film. The normal-emission spectra are composed of the Gd $4f$ core level at a binding energy of 8.4 eV, the Gd $5d/6s$ bulk bands at ~1.8 eV below E_F and the Gd

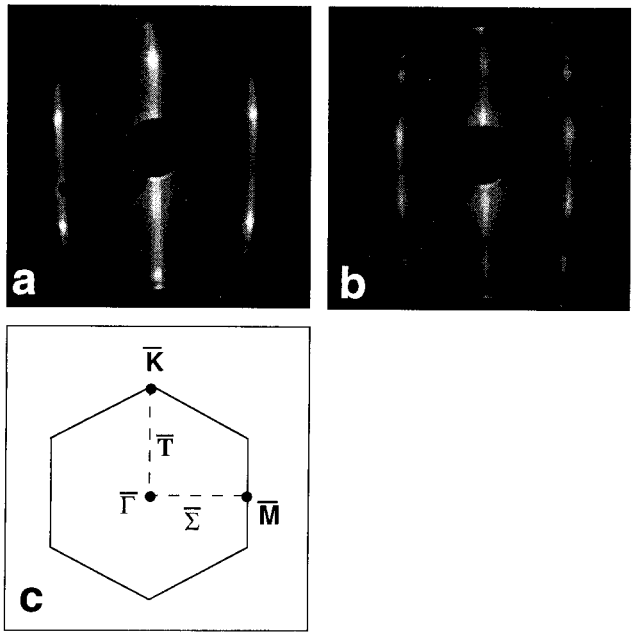

FIG. 1. The LEED pictures of a 25-Å-thick Gd film grown on Mo(112) and annealed at 650 K (a) and 480 K (b), which were acquired with electron energies of 44.6 and 58.0 eV, respectively. The LEED pattern (a) implies a hexagonal ordered structure with the surface Brillouin zone displayed in panel (c). The streaks are in the direction perpendicular to the substrate corrugations.

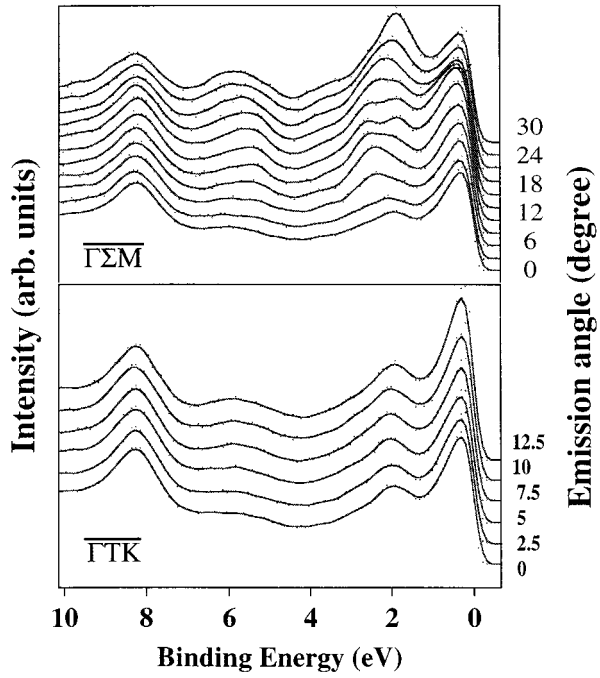

FIG. 2. The emission angle-dependent photoemission spectra of a 25-Å Gd film grown on Mo(112) along the $\overline{\Gamma\Sigma M}$ (top) and $\overline{\Gamma TK}$ (bottom) high-symmetry directions of the surface Brillouin zone. The spectra were acquired at 150 K with a photon energy of 35 eV.

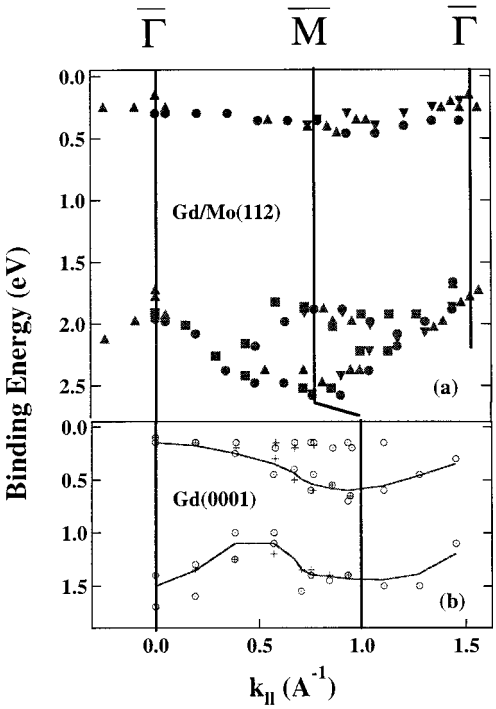

FIG. 3. (a) The band dispersion of strained Gd film along the $\overline{\Gamma\Sigma M}$ direction of the Brillouin zone. The figure was constructed from data acquired from films of 20-Å nominal thickness which were annealed to 495 K (■), 508 K (●) and 521 K (▲), as well as a 25-Å film annealed at 508 K (▼). (b) The experimental band dispersion of an ordered Gd(0001) film grown on W(110) along $\overline{\Gamma\Sigma M}$ of the surface Brillouin zone. The data was reduced from Refs. 4 and 11.

$5d_{z^2-r^2}$ surface state at ~0.2-eV binding energy. At normal emission the valence-band spectrum of the strained Gd film closely resembles the photoemission spectrum of the unstrained Gd(0001),[4,7–12] with the exception of the markedly broader surface state[9,11] ($\mathrm{FWHM}_{\mathrm{Gd/Mo(112)}}\approx 1.3$ eV, $\mathrm{FWHM}_{\mathrm{Gd(0001)}}\approx 0.2$ eV). A well-defined very intense surface state is characteristic of the clean hexagonal ordered Gd(0001) surface.[4,9,11] The broadening and suppression of the surface state of the strained Gd films may be indicative of several things: hybridization of the surface state with the bulk bands,[17] imperfect surface order, or an alteration of the symmetry of the surface, relative to the unstrained Gd(0001).

Both the $5d/6s$ bulk bands and the surface state of the dislocated and strained Gd films exhibit pronounced band dispersion (bandwidth: $\Delta E_{\mathrm{bulk}}\approx 0.8$ eV, $\Delta E_{\mathrm{surface}}\approx 0.25$ eV) along the $\overline{\Gamma\Sigma M}$ direction (parallel to the substrate corrugations) of the SBZ [Fig. 2(a)]. In contrast, the Gd $5d/6s$ valence bands are completely dispersionless along the $\overline{\Gamma TK}$ high-symmetry line (orthogonal to the substrate corrugations). The absence of the dispersion along the $\overline{\Gamma TK}$ direction, coupled with the lack of changes in the intensities with emission angle [Fig. 2(b)] indicates that the film has no long-range order perpendicular to the substrate corrugations. This is consistent with the formation of dislocations perpendicular to the corrugations, as indicated by the streaks in the LEED pattern.

The effects of strain within the thin Gd films is clearly

reflected in the reduced Brillouin-zone size of the Gd/Mo(112) films as compared to unstrained Gd(0001). The band dispersion along the $\overline{\Gamma\Sigma M}$ high-symmetry line of the strained Gd films are displayed Fig. 3(a). For comparison the band dispersion of unstrained Gd(0001) is presented in Fig. 3(b). Based on the dispersion of the strained Gd films in Fig. 3(a), we have determined the zone edge M to be at 0.77 Å^{-1}, which is smaller than that of unstrained Gd(0001) ($\Gamma - M = 1.0$ Å^{-1}).[4,5,11,12] This implies a relaxation of the hexagonal Gd structure along the substrate corrugation lines of more than 20%. This yields a relationship between the lattice vectors of Gd and Mo of 2:3 ($a_{\mathrm{Mo}}=2.73$ Å and $a_{\mathrm{Gd}}=4.09$ Å). A lattice vector relationship of n:1 has been observed for overlayers of Mg,[18] Cs,[19] and Na (Ref. 20) on the Mo(112) surface; therefore the above relationship is not without precedence.

The differences between the band structure of the strained Gd film and the unstrained Gd(0001) along the $\overline{\Gamma\Sigma M}$ direction of the SBZ are dramatic. The Gd surface state of the strained film disperses away from the Fermi level in a fashion similar to that of the surface state of well-ordered unstrained Gd films. The $5d/6s$ bulk bands of the strained Gd films, however, disperse downward (to higher binding energy with increasing wave vector), which is in the opposite direction of their counterparts in unstrained epitaxial Gd films,[7–12] which disperse upwards towards the Fermi level along $\overline{\Gamma\Sigma M}$ direction [Fig. 3(b)]. In addition, there are at least two bulk bands for the Gd/Mo(112) films. At least one band is located at approximately 1.8 eV below E_F at Γ and disperses downwards to higher binding energies away from the zone center. Two bulk bands are observed beginning approximately half way across the Brillouin zone. At the M point these two bands are separated by ~0.8 eV, where the lower band is at a binding energy of 2.6 eV.

Although the symmetry of the two bulk bands of the strained Gd films are even with respect to the mirror plane, as is the case for unstrained Gd(0001), the orbital symmetry of these two strained Gd $5d,6s$ bulk bands may still be different from that of the unstrained Gd(0001). There are several possible origins for the observed band structure of the strained Gd films: (i) The two bands may be composed of spin minority and spin majority bands, which are of $5d_{z^2-r^2}$ character, similar to the Gd(0001). Unlike the Gd(0001), however, two strained Gd bands may degenerate at the Brillouin-zone center and exhibit exchange splitting only near the zone edge, possibly due to altered magnetic ordering or reduced symmetry. (ii) The increased atomic spacing in the strained Gd may favor the wave function overlap of Gd $5d_{xz,yz}$ or $5d_{x^2-y^2}$ orbitals, rather than the Gd $5d_{z^2-r^2}$. This would suggest an assignment of the two bulk bands in the strained Gd valence band as the $5d_{xz}$ and $5d_{yz}$, and/or $5d_{x^2-y^2}$ bands, which may form a bonding-antibonding pair. One band ($5d_{x^2-y^2}$) may not be easily observed at Γ because of symmetry selection rules. (iii) The expanded Gd lattice may result in a more atomiclike valence-band structure, with a splitting of the bands into mainly $6s$ and $5d$ character near the zone edge. Our suggestions, however, leave the questions about the origin of the modified band structure of the strained Gd films unanswered. Theoretical band structures, which are lacking at this point, are needed for strained layers of Gd. We expect that the strain modified band structure may reflect changes in the magnetic properties. If theory is to be believed, these strained and expanded lattice films will remain ferromagnetically ordered as predicted by calculations by Eriksson *et al.*[22] and Harmon *et al.*,[21] rather than changing to antiferromagnetic ordering.

In conclusion we have investigated the electronic and structural properties of strained Gd films, as grown on the corrugated Mo(112) substrate. The Gd films are ordered and strained along the substrate corrugation lines, but have high densities of dislocations perpendicular to the corrugation direction, which in turn breaks down the long-range order in this direction. The strain is reflected by a hexagonal Gd structure that is expanded by at least 20% in the direction along the ''steps.'' As a consequence of strain, the Gd $5d/6s$ bulk bands disperse in the opposite direction of those of the unstrained Gd(0001). At least one band is located 1.8 eV below E_F at Γ and uniaxially disperses along $\overline{\Gamma\Sigma M}$ towards higher binding energy. Two bulk bands are observed in the vicinity of the M with a maximum energy splitting of ~0.8 eV. The strained Gd films exhibit anisotropies in the band structure and in the long-range order. We do not, as yet, know how strain will affect the magnetic ordering, or how the strain and misfit dislocations will influence the Curie or Neèl temperature of the Gd films, but these are issues of great interest.

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