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Altering the Gd(0001) surface electronic structure with hydrogen adsorption

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Hydrogen adsorption on Gd(0001) has been studied with angle-resolved photoemission. Hydrogen adsorption attenuates the surface state near E_F on the clean Gd(0001) surfaces and induces two two-dimensional bands which are at 3.8 eV and about 6 eV near $\overline{\Gamma}$. The state with the smaller binding energy has d_{z^2} character at $\overline{\Gamma}$ and disperses away from E_F about 1 eV. The state at the greater binding energy disperses toward E_F about 0.5–1 eV. At low substrate temperatures (120–130 K), the hydrogen chemisorption on the Gd(0001) surface results in a work-function decrease of 0.2 eV. The correlation between the changes in the surface electronic structure and the corresponding change of the surface magnetic ordering is discussed.

I. INTRODUCTION

Over the years, progress has been made in recognizing the role of the surface electronic structure on surface magnetic order.[1–3] One extreme example of surface magnetism is the Gd(0001) surface which exhibits enhanced surface magnetic ordering, i.e., the Curie temperature (T_c) of the surface layer occurs 20°–60° higher than that of the bulk.[4–8] Recently, insight into this unusual manifestation of surface magnetism was obtained with the discovery of a highly localized surface state near E_F in the vicinity of the Brillouin-zone center $\overline{\Gamma}$ experimentally[9,10] and theoretically.[11,12] This state has been shown to be magnetic with strong spin polarization.[13,14,11,12]

In this work, hydrogen adsorption studies were pursued to examine the relationship between the surface electronic structure and the surface magnetic order. Previous work by Cerri, Mauri, and Landolt[15] has shown that the surface magnetic order of the Gd films deposited on a Fe(001) substrate is suppressed substantially by even a small amount of hydrogen adsorption [say, 0.5 L (1 L=10^{-6} Torr sec)]. A correlation between the magnetic measurements and electronic structure can therefore be investigated.

Hydrogen adsorption on various metal surfaces has been studied by many groups with a slightly different emphasis.[16] Hydrogen adsorption and/or absorption is technologically important in heterogeneous catalysis, hydrogen storage, and embrittlement. It has also been studied because of the presumed simplicity of hydrogen as an adsorbate having only one $1s$ electron. There are, however, few studies of hydrogen adsorption on rare-earth surfaces at a fundamental level on well-ordered and well-characterized surfaces. Such rare-earth surfaces have been achieved only recently, because great care must be paid to sample preparation to obtain a characteristic surface state near E_F on Gd(0001) (Refs. 9 and 10) and Tb(0001).[17] In this work, we will present the adsorption kinetics and the work-function change of the hydrogen chemisorption process, along with the H-induced surface electronic structure. At saturation, hydrogen adsorbs into the 1 × 1 structure of a Gd(0001) lattice. Using the dipole selection rules for photoemission, we postulate the site of hydrogen adsorption.

II. EXPERIMENTAL

The experiments are carried out in an UHV system equipped with an angle-resolved electron analyzer for photoemission and a reverse view low-energy electron diffraction (LEED) system.[18] The light source used for the photoemission study was the 1-GeV ring at the Synchrotron Radiation Center in Stoughton, Wisconsin, with the light dispersed by a 6-m toroidal grating monochromator. The incident light of 38° or 66° off normal was used to provide a 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 ($\overline{\Gamma}$) or off-normal along $\overline{\Gamma\Sigma M}$ and $\overline{\Gamma TK}$ of the Gd(0001) surface Brillouin zone. The combined (including the monochromator and electron energy analyzer) photoemission energy resolution was 0.15–0.2 eV, while the angular resolution was ±1.5°. The binding energies in this work are referenced to the Fermi level. The work-function change was measured in the usual way by measuring the kinetic-energy cutoff of the photoemission spectra on a biased (10 V) sample.

Clean and well-ordered Gd(0001) surfaces have been prepared *in situ* by slowly depositing Gd onto the W(110) substrate at room temperature under the vacuum in the 10^{-11} range as described elsewhere.[9,19] All the data used in the current work were taken for thick Gd films (typically ≥ 40 Å) for which the bulk bands of Gd(0001) are well developed.[9,10] The Gd(0001) crystalline films were exposed to hydrogen by admitting high purity H_2 gas through an UHV-compatible leak valve, and the exposures were measured in units of langmuirs, uncalibrated for an ionization gauge cross section. The exposure was done at a H_2 pressure of 10^{-8} or lower. Adsorption was undertaken on samples both at 120–130 K and at 300 K. Surface order was examined with LEED.

III. THE HYDROGEN ADSORPTION PROCESS

Photoemission spectra taken at normal emission from Gd(0001) at 120 K with increasing exposure to hydrogen are shown in Fig. 1. The feature at 8.4-eV binding energy is the Gd $4f$ state, while the features next to E_F and at 1.6–1.7 eV below E_F are a Gd $5d$ surface state and bulk bands, respectively.[9,10] The feature which appears at E_b=3.8 eV with a full width at half maximum (FWHM) of 0.4 eV at normal emission is a new state induced by hydrogen adsorption.

The intensity of the new H-induced state increases as that of the surface state near E_F decreases, and both the features eventually cease changing in intensity with hydrogen exposures of about 3 L at 120 K, when the surface state near E_F disappears. This was taken to indicate that the surface adsorption sites could be saturated with a monolayer of hydrogen atoms. With hydrogen exposure, the Gd bulk bands are less affected, indicating that the hydrogen atoms tend to adsorb only into one layer at or near the surface (at least for low-temperature adsorption). Thus hydrogen chemisorption alters the electronic properties of the surface with minimum effect to the bulk.

The relative intensities of both the H-induced state and the Gd $5d$ surface state for 120-K adsorption were plotted out in Fig. 2(a) for different exposures. Since hydrogen adsorbs only at the Gd surface and the mean free path of electrons in hydrogen is large, the intensity of Gd $4f$ remains constant during the exposure sequence. Therefore, the intensity of the H-induced state relative to

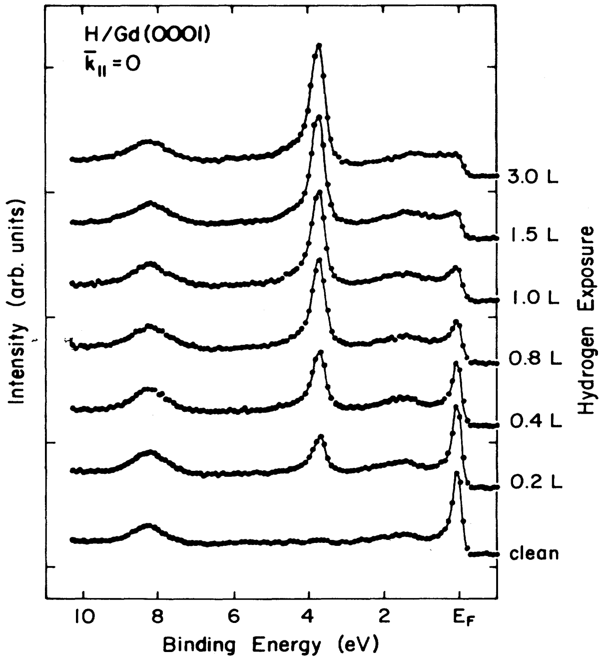

FIG. 1. Typical spectra of the hydrogen on a Gd(0001) surface taken at normal emission under a sequence of hydrogen exposure onto the 120-K substrate. The photon energy is 33 eV. The light incident angle onto the Gd surface is 66°. The $5d$ surface state for the clean Gd(0001) and the H-induced state coexist at the intermediate coverage with one attenuating and the other saturating.

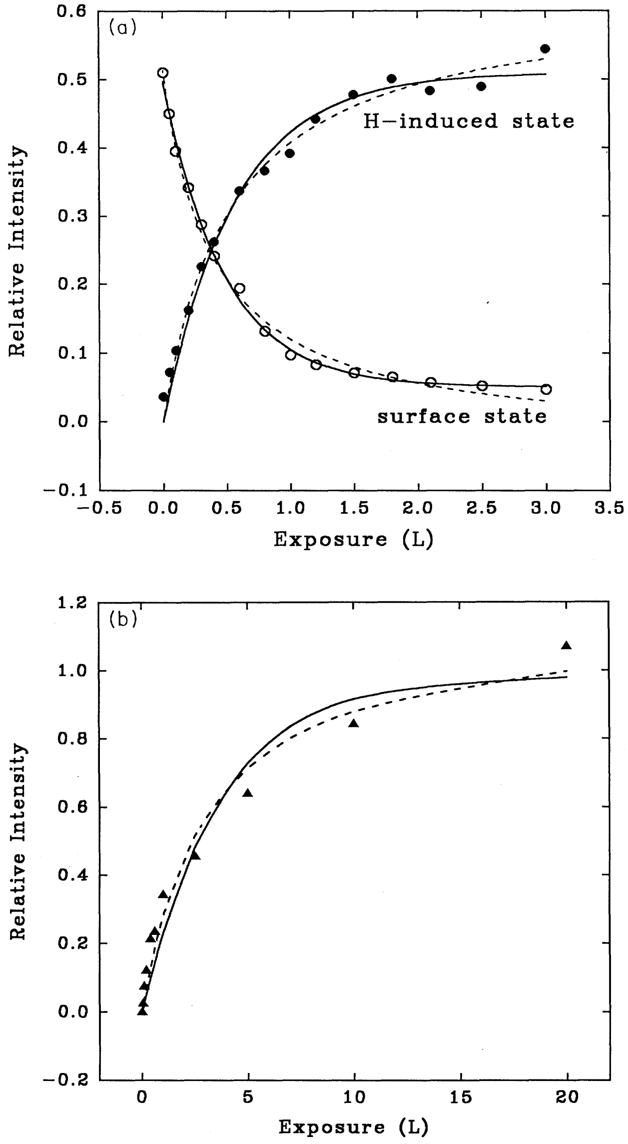

FIG. 2. Relative intensities (normalized with the Gd $4f$ intensities) of the H-induced state at 3.8 eV and the Gd $5d$ surface state changes with hydrogen exposure. The solid and dashed lines are the fitting results assuming the first- and second-order Langmuir-type adsorption isotherms, respectively. (a) Low-temperature adsorption (120 K); (b) room-temperature adsorption (300 K).

that of Gd $4f$ should be a good measure of the absolute hydrogen coverage θ with the relative intensity at saturation corresponding to one monolayer (θ=1). A similar correlation between the intensity and coverage can also be obtained from the attenuation of the clean Gd $5d$ surface state. The resulting coverage θ versus exposure data were fitted with a Langmuir-type adsorption rate equation, common to chemisorption,

$$R = S_0 N(1-\theta)^n = SN,$$

where R is the adsorption rate, S and S_0 are the sticking coefficient and initial sticking coefficient, respectively. N is the hydrogen impingement rate at the surface. The fitting results using Langmuir adsorption isotherms are shown as the solid ($n = 1$, normal for monoatomic gases) and dashed lines ($n = 2$, to occupy two adjacent sites, common with diatomic gases) in Fig. 2(a). While the scatter of the data prevents us from determining the value of n experimentally, the generally good fits suggest that the adsorption onto the Gd(0001) substrate at low temperature is the Langmuir type with only one dominant adsorption site. Notice that the fitting parameters for the attenuation of the surface state on a clean surface is the same as that for the saturation of the H-induced state within the experimental error. This further suggests that our assumption that those intensities are linearly correlated with coverage is reasonable. There is no indication of a highly mobile precursor state. The activation barrier for this dissociative chemisorption to occur should be lower than the room-temperature thermal energy (0.02 – 0.03 eV), if any.

The adsorption onto the room-temperature substrate, however, behaves slightly differently [see Fig. 2(b)]. The intensity of a hydrogen-induced state saturates at a much higher exposure compared to that on the low-temperature substrate. The fitting of the data with the Langmuir rate equation [shown as the solid and dashed lines in Fig. 2(b)] does not yield a satisfactory result. The difference between the adsorption on a Gd(0001) surface at 120 K and at 300 K can be more readily seen from the the estimated sticking coefficients S (the graphic derivatives of the coverage versus exposure curve) versus coverage (see Fig. 3), where the coverage θ is again obtained from the relative intensities of the H-induced state. The coverage dependence of the room-temperature sticking coefficient implies that the simple single-site adsorption picture valid at 120 K is not valid at 300 K. The absolute initial sticking coefficients for room temperature and low temperature are very similar, suggesting the prime bonding site is the same for room temperature and low temperature. This is consistent with the fact that hydro-

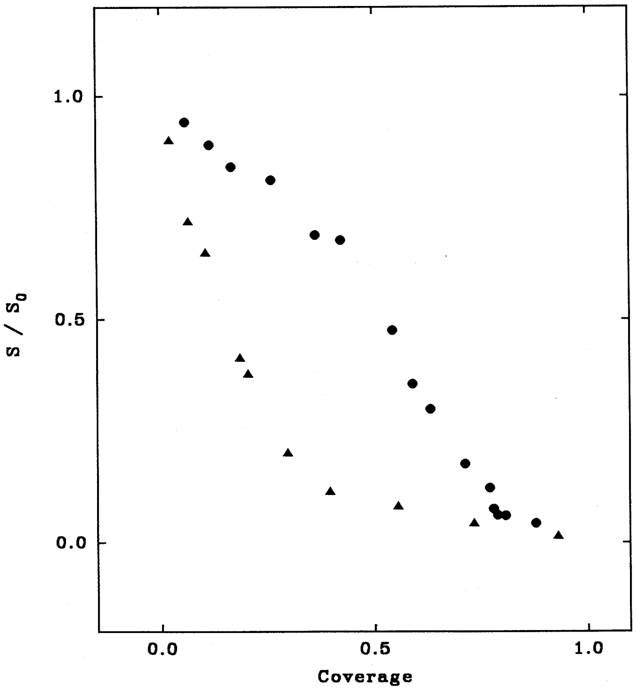

FIG. 3. Relative sticking coefficient vs the hydrogen coverage. •, room-temperature (300 K) adsorption; △, low-temperature (120 K) adsorption.

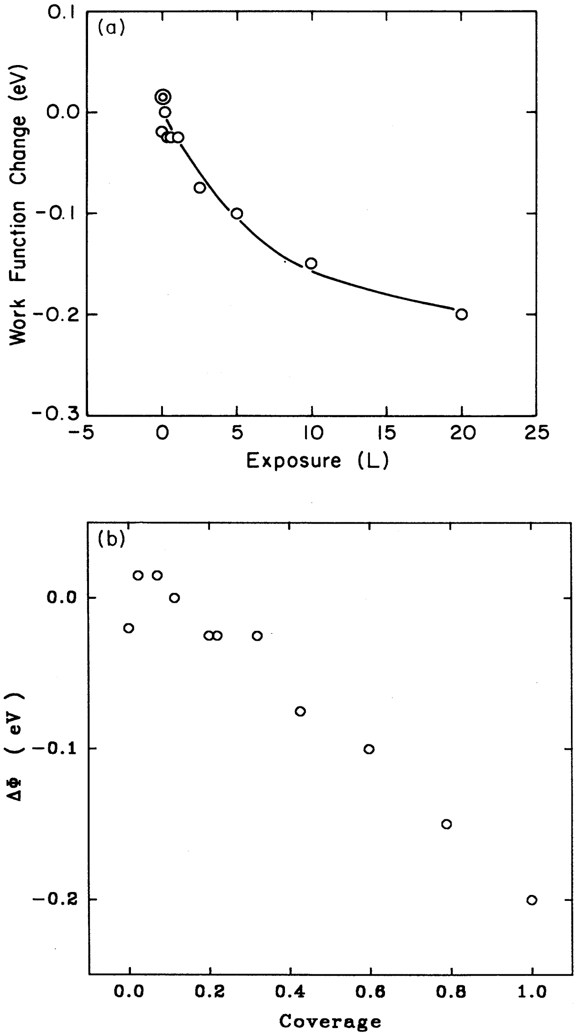

FIG. 4. Hydrogen-induced work-function change $\Delta\Phi$. The experiment was done at room temperature.

gen atoms on the rare-earth surfaces start to diffuse into the bulks when $T \geq 195$ K.[20]

Hydrogen-induced work-function changes have been measured from the cutoff shift during hydrogen exposure (Fig. 4). The work function of clean Gd(0001) is measured as 3.3 ± 0.1 eV, the same as in previous measurements.[21] The total work-function change after saturation is -0.21 ± 0.05 eV. This is consistent with the model of dissociative chemisorption of hydrogen at the Gd(0001) surface but not hydride formation. There is no visible Gd $4f$ core-level shift, which also contradicts the existence of any hydride. The work-function changes $\Delta\Phi$ follows a nearly linear relationship with respect to the hydrogen coverage as seen in Fig. 4(b), indicating a weak dipole-dipole interaction. Using the Helmholtz equation (ignoring the dipole-dipole coupling)

$$\Delta\Phi = -\mu_0 \frac{\sigma_0}{\epsilon_0},$$

and assuming the H and Gd ratio on the surface is 1:1, the dipole moment induced by hydrogen chemisorption is $0.013e$ Å (0.062 Debyes).

IV. THE HYDROGEN-INDUCED BAND STRUCTURE ON GD(0001)

The surface Brillouin zone is shown in Fig. 5. Figure 6 contains several typical photoemission spectra along the $\overline{\Gamma\Sigma M}$ direction of the Gd(0001) surface Brillouin zone. Two points are readily seen: (1) The H-induced feature observed at $E_b = 3.8$ eV at $k_{\parallel} = 0$ disperses away from E_F (higher binding energy) for $k_{\parallel} \neq 0$. (2) Another weaker feature emerges away from normal emission. From Fig. 7 it is clear that the intensities of both of these two marked new features increase with H_2 exposure, indicating they are both induced by hydrogen adsorption.

When compared with the data for clean Gd(0001),[9] the two H-induced features have binding energies larger than any of the bulk bands of clean Gd observed throughout the Brillouin zone. So the two states are in a gap of the projected bulk band structure of Gd. The hydrogen-induced state at a smaller binding energy (3.8 eV at $\overline{\Gamma}$) is a two-dimensional state since its binding energy exhibits no dispersion with different perpendicular wave vectors $\mathbf{k}_{\perp}$ across the bulk Brillouin zone of Gd along the Γ-A direction. The two-dimensionality of the second H-induced feature is also obvious from the two-dimensional band structure, since as the other H-induced band, this state follows exactly the same band dispersion for the different

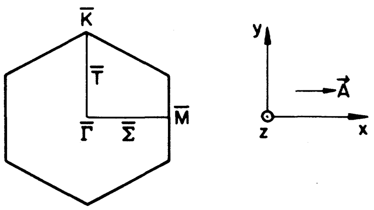

FIG. 5. Gd(0001) surface Brillouin zone. The vector potential **A** is in the x-z plane.

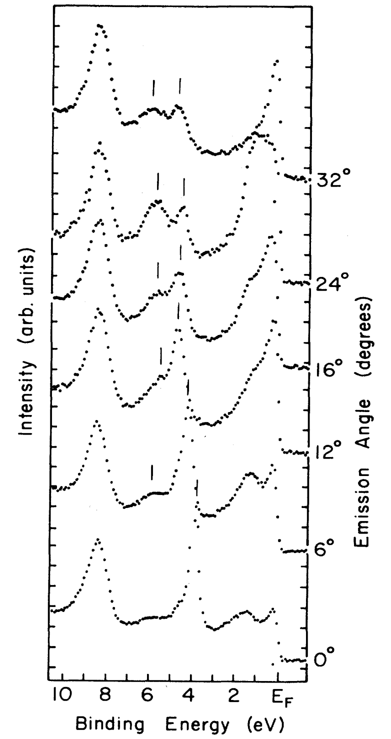

FIG. 6. Typical off-normal emission spectra of H/Gd(0001) along $\overline{\Gamma\Sigma M}$ of the Gd(0001) surface Brillouin zone. The photon energy is 38 eV. The light incident angle is 38°. The vector potential **A** of the light is in the scattering plane, i.e., the even geometry. Band dispersion is apparent for the two hydrogen-induced features, as marked in the figure.

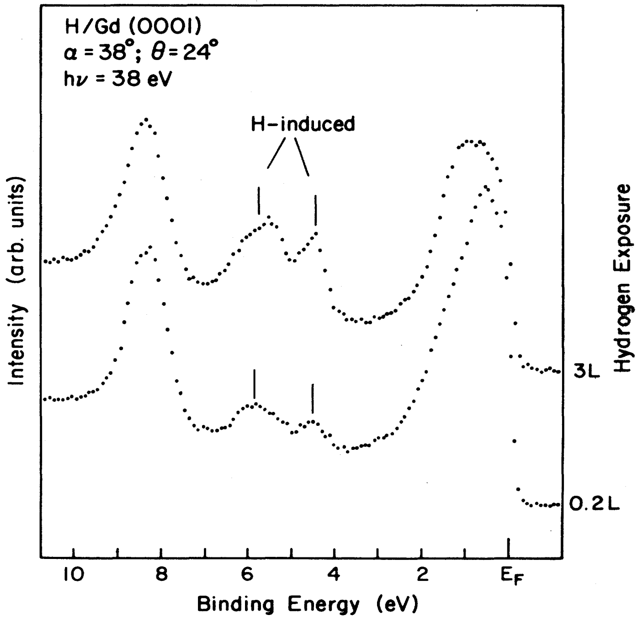

FIG. 7. Photoemission spectra taken with photon energy of 38 eV and electron emission 24° off normal. The intensities of the two marked features increase with hydrogen exposure.

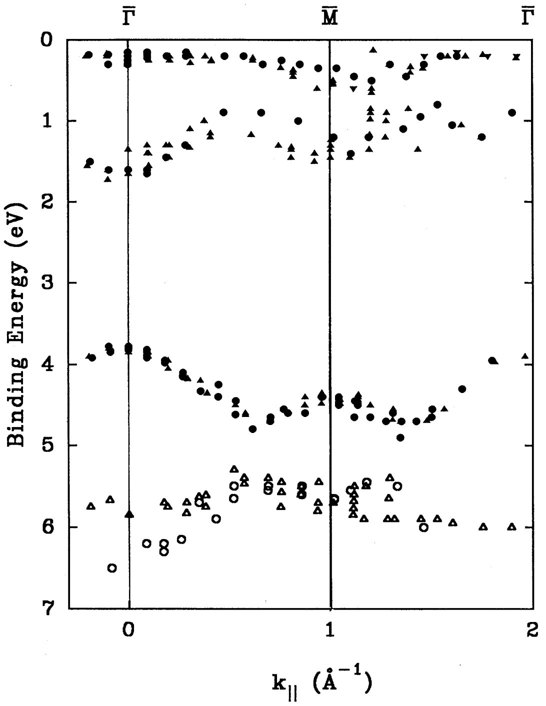

FIG. 8. Experimental two-dimensional band dispersion of H/Gd(0001) along $\overline{\Gamma\Sigma M}$ of the Gd surface Brillouin zone for even geometry, with the photon energies of 33 and 38 eV. The solid circles are taken with room-temperature adsorption while the triangles are for low-temperature adsorption (120 K).

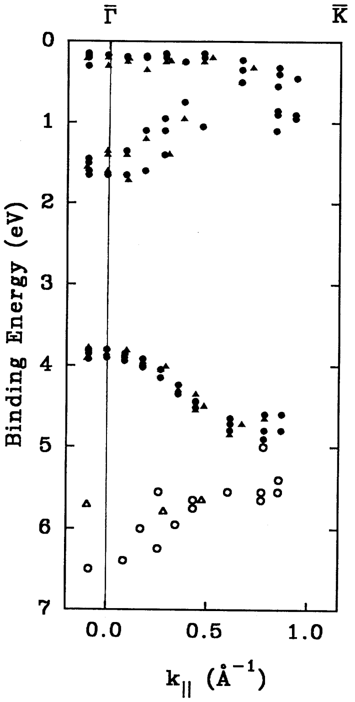

FIG. 9. Experimental two-dimensional band dispersion of H/Gd(0001) along $\overline{\Gamma T K}$ of the Gd surface Brillouin zone for odd geometry, with the photon energies of 33 and 38 eV. The solid circles are taken with room-temperature adsorption while the triangles are for low-temperature adsorption (120 K).

photon energies of 33 and 38 eV (Figs. 8 and 9). This confirms our hypothesis that hydrogen chemisorption, under our experimental condition, is restricted to the surface.

From several sets of data, including results for different photon energies (33 and 38 eV) as well as results at different hydrogen coverages, the hydrogen-induced band structure has been mapped out in Figs. 8 and 9. Figure 8 shows the bands along $\overline{\Gamma\Sigma M}$ of the surface Brillouin zone with even geometry (the vector potential of light **A** in the scattering or emission plane) while Fig. 9 is along the $\overline{\Gamma T K}$ direction with odd geometry (the vector potential of light **A** perpendicular to the scattering or emission plane). While most of the band dispersion data was taken at hydrogen saturation, or near saturation coverage, the features and their dispersion are qualitatively the same for the coverage at least as low as $\theta = 0.4$. This suggests hydrogen atoms form "islands" on the Gd(0001) surface.

Both of the two H-induced bands disperse dramatically. This is in contrast with the highly localized surface state of clean Gd(0001), which has little dispersion with $k_{\parallel}$ near the zone center until emerging into the bulk bands. Band dispersion directly implies that there is an electron wave-function overlap for nearby atoms in the surface plane, or itinerancy of the electrons. Our data suggest that the surface valence electrons become less localized upon hydrogen adsorption. As discussed in a latter part of the paper, this tends to decrease the magnetic coupling in the surface layer.

The Gd $5d$-$6s$ bulk bands at binding energies of 1–2 eV are not expected to be symmetric with respect to the surface Brillouin-zone boundary. This is a consequence of the fact that with the change of emission angle, the $k_{\perp}$ of the bulk is also changed. Thus in Fig. 8 there is a large scattering of the data for these bands because of the data sets taken with different photon energies (different $k_{\perp}$).

The H-induced surface state at 3.8 eV is in fact the same state as the surface state on a clean surface, which can be demonstrated from the symmetry character and partial photoionization cross section of the two states. The symmetry character of the bands was determined by varying the light polarization and through the use of the dipole selection rules. Figure 10 shows the two normal emission ($k_{\parallel} = 0$) spectra taken on the same H/Gd(0001) system with more p-polarized light ($\alpha = 66°$) and more s-polarized light ($\alpha = 38°$). It is clear that the upper H-induced feature at 3.8 eV in binding energy is strongly enhanced by p-polarized light. The symmetry of this H/Gd(0001) surface system should form a space group containing the point group of C_{3v} or C_{2v}. The $E_b = 3.8$ eV state therefore can only have the character of s or d_{z^2} ($6s^2 5d^1$ for Gd) at the zone center, the same as that of the surface state near E_F on the clean Gd(0001). The narrow width of this feature suggests it is a state with mainly high angular momentum, namely, the $5d$ state. Our constant initial state (CIS) results (Fig. 11) indicate that the partial photoionization cross section (normal-

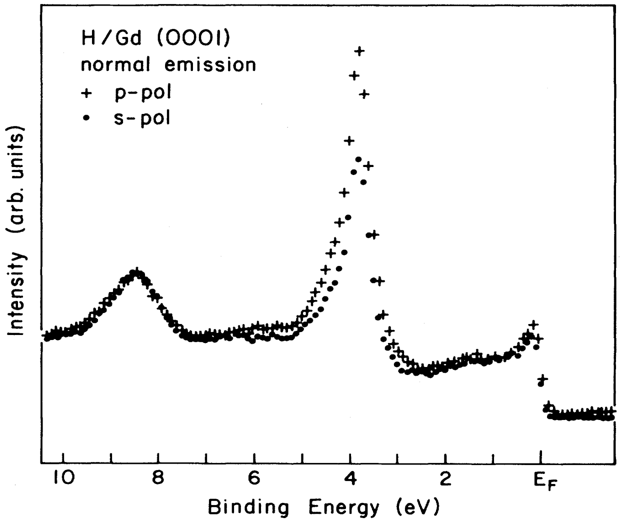

FIG. 10. Photoemission spectra taken with light incident angles of 66° (with more *p*-polarized light) and 38° (with more *s*-polarized light). The H-induced state at 3.8 eV is proven to have Δ_1 character. The photon energy was 33 eV.

ized for the photon flux with a gold diode photocurrent) of the H-induced feature at 3.8 eV at normal emission exhibits a very similar resonance around 33-eV photon energy compared to the clean Gd surface state. There is no resonance at this initial energy before adsorbing hydrogen onto clean Gd surfaces. This indicates that this state has a significant amount of Gd 5*d* character. We can therefore say that the clean Gd 5*d* surface state is "converted" into the hydrogen-induced surface state at 3.8 eV in the sense that these two states both have the same Gd $5d_{z^2}$ character and the former one loses intensity while the latter gains intensity during hydrogen exposure.

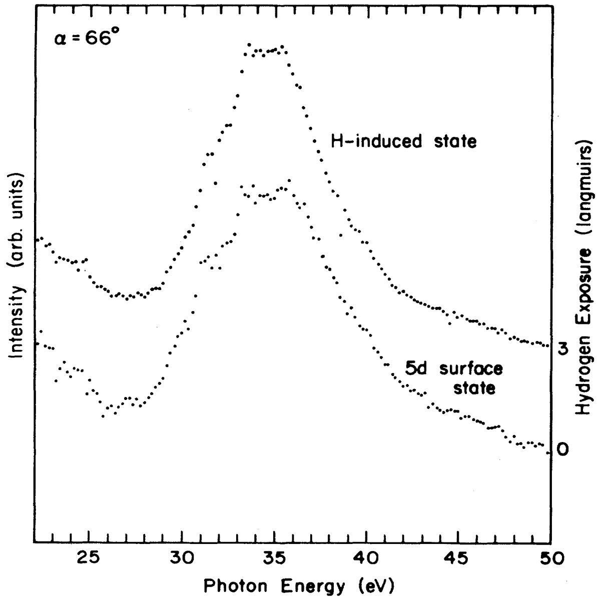

FIG. 11. Constant initial state (CIS) spectra taken at normal emission by scanning the photon energy and the electron kinetic energy simultaneously. The initial states are the Gd 5*d* surface state on the clean surface and the H-induced state at 3.8 eV on the hydrogen saturated surface to measure their partial photoionization cross section. The light incident angle α is 66°.

As seen in Fig. 8, the two H-induced bands retain the Brillouin zone of the Gd(0001) surface along the $\overline{\Gamma\Sigma M}$ direction. This is consistent with the observation of the 1 × 1 structure in LEED when exposing H_2 onto the Gd(0001) surface at 120 K. Although many H/metal systems undergo a surface reconstruction, it does not appear to occur for Gd(0001). The surface structural ordering is retained although the electronic structure is severely altered with hydrogen adsorption. No information about a possible change in surface relaxation can be obtained from our data.

V. DISCUSSION

A. Possible adsorption sites

From our photoemission data, we can postulate possible adsorption sites for hydrogen atoms on Gd(0001) surfaces. The two H-induced bands disperse toward each other when increasing $k_{\|}$ while leaving the center of the bands almost fixed. This suggests that they are a pair of bonding-antibonding states at least in the surface plane, although the bonding for perpendicular direction may be different.

The hydrogen atoms are localized near the surface as indicated by the two-dimensional character of the H-induced bands. Our data do not support the atop-site adsorption configuration. If that were the case, it is likely that the H 1*s* electrons hybridize with the most extended wave functions in the perpendicular direction, Gd $5d_{z^2}$ states, to form the bonding state. As a result, there should be significant intensity for the lower band (bonding state) at its lowest point, which occurs at $\bar{\Gamma}$. Instead, we only see significant intensity at $\bar{\Gamma}$ in the upper band (with smaller binding energy of 3.8 eV), where the state has the character of d_{z^2}. This indicates that d_{z^2} electronic bands, though strongly disturbed, do not directly contribute to the bonding. This rules out the possibility of hydrogen atoms adsorbing onto the top sites.

Our data are more consistent with the hydrogen atoms adsorbing at the threefold hollow sites or the twofold bridge site, at the surface or subsurface. At $\bar{\Gamma}$, the symmetry is high (C_{3v} for the fcc or hcp hollow sites, C_{2v} for the bridge site with only one of the three sites occupied). The two bands we observed are far apart either because of the different symmetry characters of the bands, or because the two H-induced bands share the same symmetry at $\bar{\Gamma}$ but form a bonding-antibonding pair as in the case of hydrogen on Ti(0001).[22] Along the $\bar{\Sigma}$ line of Gd(0001), the symmetry is lowered and the 1*s* orbital of hydrogen is allowed to mix with any of the $5d_{x^2,y^2,z^2,xz}$ or 6*s* orbitals of Gd to form the hybrid band and bonding. The bonding is likely formed by the hybridization of H 1*s* and Gd $5d_{x^2\pm y^2,xz}$. At the same time, since the two states are in the same group representation (the symmetric one), the two bands tend to disperse toward each other as symmetry mixing occurs for the various rectangular representations. When the $\overline{M}$ point is reached, the symmetry becomes higher again (C_{2v}). So at $\overline{M}$ the bands are expected to be more separated from each other again. Alternatively, the bonding-antibonding bands cross each other, and the apparent gap between the two H-induced bands may be a result of the spin-orbit interaction present in this large-Z system of gadolinium. Along the $\overline{T}$ direction, the measurements were taken in odd geometry. The fact that the dispersion is very similar to that along the $\overline{\Sigma}$ direction may suggest that there are different domains at the surface as Feibelman suggested for H/Be(0001),[23] and we therefore are <u>not</u> measuring the odd-symmetry band structure.

Our arguments to the adsorption site are mainly based on symmetry arguments. The analysis ignores the spin-orbit interaction. In addition, it is not clear how the two fully occupied bands we observed are formed at relatively high binding energies. Theoretical calculations, for both the band dispersion and total energy of the different sites will be useful in gaining further insight into this system. Experimental studies on the absolute hydrogen coverage and hydrogen bonding site will be valuable.

B. Comparison with hydrogen on other metal surfaces

For Ni(111),[24] Pd(111),[24] and Cu(111),[25] both the surface state on the clean surface and the split-off bonding state continuously shift in binding energy with hydrogen adsorption, indicating that the hydrogen atoms affect the surface electronic structure in a very delocalized fashion. In contrast, hydrogen adsorption on Gd(0001) produces new states at the fixed binding energies, which coexist with the attenuating surface state of the clean Gd(0001). This implies that the effect introduced by the hydrogen atoms is very local. It is consistent with the nearly linear coverage dependence of the work-function change. This is, in some sense, a local bond picture since the adsorption site of hydrogen atoms has to be well defined and nonmobile, although the actual bonding occurs through dispersive electronic bands. Combining the fact that the band dispersion is 1 × 1 at different coverages and the "localized" nature of the hydrogen interaction with Gd atoms, it is most likely that hydrogen atoms start to form 1 × 1 ordered islands even at the relatively low coverage. Such a "local" picture is consistent with the spatially localized surface state of the clean Gd(0001).[11,12] Recently, a similar effect of hydrogen islands formation is also observed on the Be(0001) surface.[26]

Of the many H/metal systems investigated, the cases most like H/Gd(0001) are H/Ti(0001) (Refs. 22 and 27) and H/Sc(0001),[27] where a good agreement of the theoretical chemisorption calculation and the experimental angle-resolved photoemission spectroscopy (ARPES) measurement was observed.[22] For H/Ti(0001), the two distinct H-induced bands show a similar trend of band dispersion as is the case for Gd(0001). The H-induced $\Delta\Phi$ are about -0.2 eV for both Gd(0001) and Ti(0001). Such a similarity is because of their similar crystal structure (hcp) and the outermost electron configuration (d^2s^2 for Ti and d^1s^2 for Gd). It is likely that the chemisorption of hydrogen on Gd(0001) can well be understood in the general picture presented for Ti(0001). If the upper band is the antibonding state as indicated for Ti(0001),[22] then the H–Gd bonding (with the two bands separated by 2.2 eV at $\overline{\Gamma}$) is weaker than H–Ti bonding (where the two bands are separated by 5.7 eV at $\overline{\Gamma}$). H adsorbs onto the threefold hollow sites of the Ti(0001) surfaces.

C. Remarks on surface magnetism

On Gd(0001), hydrogen atoms do not alter the geometric arrangement of Gd atoms in the surface plane. Instead, hydrogen disturbs the surface electronic structure dramatically, namely, to "convert" the highly localized surface state on the clean surfaces into a much more dispersive surface state and introduce a new state split off from the bulk band to form the bonding state. This is accomplished with the bulk bands much less altered. The goal of introducing controlled changes in the surface electronic structure to study its relation with magnetic order is therefore reached. While a detailed connection between such a surface electronic structure and the magnetic properties must await theoretical band-structure calculations, our data suggest the origin of the suppressed magnetic order for hydrogen-covered Gd surfaces.[15] As a consequence of the highly dispersive bands formed upon hydrogen adsorption, we believe the magnetic coupling in the surface layer is decreased. There is a possible concomitant reduction in the magnetic moment (conduction-electron part only) caused by a drop in the density of states near E_F.

As a prototypical localized magnetic system, it is well known that for gadolinium, the magnetic coupling among the magnetic moments of the atoms is via indirect coupling.[28,29] The large local magnetic moment from Gd $4f$ electrons ($7\mu_B$) has no wave-function overlap with the $4f$ electrons on the adjacent atoms as demonstrated by Fig. 12. Instead, $4f$ electrons will only have an exchange interaction with the valence- and/or conduction-band electrons. This partially polarizes the valence and/or conduction electrons, contributing about a moment of $0.63\mu_B$ to the bulk Gd. It is the delocalized valence and/or conduction electrons, especially the $5d$ electrons in the case of Gd,[30] that magnetically couple the nearby atoms. From Fig. 12 it is easy to see that the overlap, and therefore the exchange interaction, between the $5d$ and $4f$ electrons will increase when the $5d$ electrons become more spatially localized. The fact that there is a highly localized surface state on the clean Gd surfaces and highly dispersive surface states on hydrogen-saturated surfaces suggests enhanced magnetic coupling in the former case and reduced coupling in the latter, between the $4f$ and $5d$ electrons. Theoretical studies of the semi-infinite Ising systems[31] suggest that the magnetic coupling in the surface layer (J_s) is the main factor to affect the surface magnetic order. Enhanced surface magnetic order can occur only when $J_s > J_{sc}$.[31] When $J_s < J_b$, the surface becomes magnetically soft to spin-wave exci-

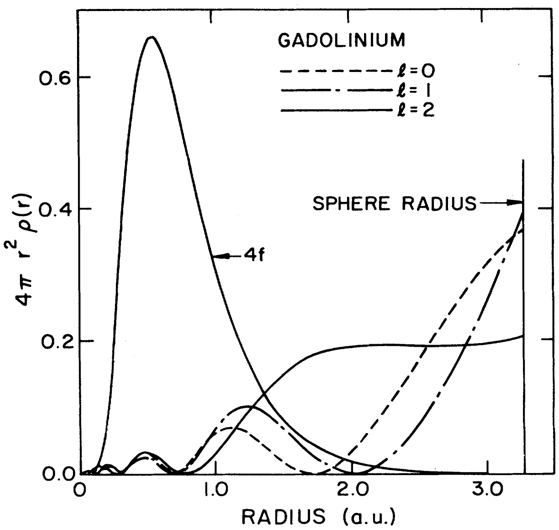

FIG. 12. The calculated radial charge densities of $4f$, $5d$, and $6s$ electrons in the Wigner-Seitz sphere of Gd metal, taken from Ref. 30.

tations and results in suppressed surface magnetic order at finite temperature. Our results are consistent with enhanced surface magnetic ordering on clean Gd surfaces and suppressed surface magnetic ordering on hydrogen-saturated Gd surfaces.[15]

For this kind of indirect coupling in the rare-earth metals, the net magnetic moment of the conduction electrons can be estimated as proportional to the density of states at E_F.[32] From our results, it is clear that the density of states near E_F is significantly reduced with hydrogen adsorption because of the destruction of the surface state near E_F. Therefore, the magnetic moment of the conduction electrons is likely lower than the case for the clean surfaces, though a comparison with the magnetic moment in the bulk is hard to make. Nevertheless, the total magnetic moment will not change significantly since it is mainly formed by the localized $4f$ electrons.

VI. CONCLUSION

We have studied hydrogen adsorption on Gd(0001) surfaces. Hydrogen adsorption on gadolinium is a dissociative chemisorption process that occurs at the surface. Unlike on several transition metal surfaces, hydrogen atoms tend to form 1 × 1 islands and affect the Gd surface in a "local" fashion. We have mapped out the two-dimensional hydrogen-induced bands along the $\overline{\Gamma\Sigma M}$ and $\overline{\Gamma T K}$ lines of the Gd(0001) surface Brillouin zone. The surface state near E_F is destroyed and replaced with a highly dispersive H-induced state. The split-off bonding state was observed at about 6 eV near $\overline{\Gamma}$ and disperses upward for about 0.5–1 eV. The bonding site is postulated as the threefold hollow or the twofold bridge site in the overlayer. The differences on the magnetic properties of the Gd bulk, clean surface, and H-saturated surface can be understood in terms of electronic structure, and such a comparison provides a good example on how the magnetic ordering is controlled by the electronic structure.

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