PHYSICAL REVIEW B **73**, 174423 (2006)

Surface structure of CO on Co/Pd(111) magnetic thin films and its effect on the spin reorientation transition of the film

Daiju Matsumura,* Kenta Amemiya, Soichiro Kitagawa, Toru Shimada, Hitoshi Abe, and Toshiaki Ohta†
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Hirokazu Watanabe and Toshihiko Yokoyama
Institute for Molecular Science, Myodaiji-cho, Okazaki, Aichi 444-8585, Japan

(Received 27 October 2005; revised manuscript received 1 February 2006; published 18 May 2006)

The CO surface structures on Co/Pd(111) magnetic thin film and the chemisorption-driven spin reorientation transition have been studied by soft x-ray spectroscopies. C 1*s* photoelectron diffraction for CO/Co/Pd(111) revealed that CO is adsorbed both on the atop and bridge sites at 200 K, while CO is adsorbed exclusively on the atop site at 300 K. From simultaneous measurement of C 1*s* photoelectron spectroscopy and Co *L*-edge x-ray magnetic circular dichroism during stepwise CO adsorption and annealing, it was concluded that the spin reorientation transition is induced not by a thermodynamical effect but by the CO adsorption on the bridge site. These results show that the adsorption structure has a significant effect on the surface magnetic anisotropy of the thin film.

DOI: 10.1103/PhysRevB.73.174423 PACS number(s): 75.70.Ak, 75.30.Gw, 68.43.Fg, 79.60.Dp

I. INTRODUCTION

Many efforts have been made for exploring the structural and magnetic properties of magnetic thin films both from the scientific and technological points of view because they represent a typical low-dimensional physical state and have potential applications for a magnetic recording media. Among several characteristic properties of the magnetic thin films, magnetic anisotropy is one of the most interesting features. The electron spin itself has no preferential orientation, but in crystalline magnets it has a magnetocrystalline anisotropy via the spin-orbit interaction with the electron orbital. Magnetic anisotropy is generated not only by intrinsic properties, but also by extrinsic factors, such as shape effects and the condition of preparation. Shape anisotropy always favors an easy axis parallel to the surface because of the classical electromagnetic demagnetizing field. However, some magnetic thin films have a perpendicular magnetic anisotropy (PMA) as a result of the competition among many effects which originate from the surface, interface and bulk.[1–5] Many studies have been reported on PMA to solve the complicated mechanism of this phenomenon.

Co thin films prepared on Au, Pt, and Pd(111) surfaces are known to exhibit the PMA only below a few monolayer (ML) thickness regime.[1,2,6–11] For multilayer samples, the PMA is observed in a wider thickness range. Thus, it is supposed that the PMA originates from the interface between Co and nonmagnetic metal layers.[12,13] On the other hand, in the surface of magnetic thin films, one can expect a different anisotropy due to the orbital magnetic moment. Since there is no atom above the surface, the out-of-plane electron orbital is less quenched by the crystal field than in-plane one. Large in-plane magnetic anisotropy, created by out-of-plane electron orbitals, must exist at the surface. Thus, we are convinced of the importance of studying the magnetic anisotropy of the thin films at the surface.

Some attempts have been made to control the magnetic anisotropies of thin films by surface perturbations. It was found that the gaseous adsorption on the surface often changes the magnetic anisotropy of the film and induces a spin reorientation transition.[14–19] In fact, the adsorption of molecular gases, such as CO, NO, and O_2 on a Co thin film on Pd(111), induces a change of the magnetic easy axis of the Co thin film from surface parallel to perpendicular direction, as studied by using x-ray magnetic circular dichroism (XMCD) in absorption spectroscopy.[20,21] It was also found that CO adsorption on a 3.5–6.5 ML Co film on Pd(111) causes the spin reorientation transition at 200 K, but not at 300 K.

For such case, the surface structures of adsorbates can represent the significant information about the magnetic properties of the magnetic thin film. The surface structures of CO molecule on the metal surfaces have been widely studied in the field of surface science.[22–24] In many systems, CO is adsorbed by the end of carbon atom and keeps the molecular axis perpendicular to the surface. However, the coordination structure at the metal-carbon bonding shows all of atop, bridge and hollow types for many systems in compliance with the coverage, temperature and the condition of the surface.[22–24] For this case of CO on Co/Pd(111), in order to clarify the mechanism of the effect of adsorbates on the surface magnetic anisotropy, the surface structure of CO should be determined. Although the adsorption structures on the single crystal surfaces have been determined in many systems, it is difficult to apply these structures to the thin film systems because the surface structure of adsorbates on thin films is not always equal to that on single crystal surfaces of the same substance.[25] In this paper, we address the adsorption structures of CO on the Co/Pd(111) thin film by x-ray photoelectron diffraction (XPD) in the scanned-energy mode at 300 K and 200 K. XPD is a powerful tool for resolving the surface structure of adsorbates because XPD is an element selective method and can detect the metal-adsorbate bonding directly. Especially in the scanned-energy mode, the quantitative parameters of the structure can be obtained by using the synchrotron radiation.[26,27]

On the other hand, for clarifying the relation between the CO surface structures and the magnetic anisotropies of the Co thin film, it is quite necessary to obtain both the structural and magnetic information in the same condition. Chemical shift in x-ray photoelectron spectroscopy (XPS) is useful for observing the rough surface structure in short time.[23] We have already developed the system in which XPS and XMCD in absorption spectroscopy can be taken in the same condition and reported the results of the relation between the dosage and the magnetic easy axis in the past report.[28] In this paper, we show the precise correlation between the surface structures of CO and the magnetic anisotropies of the Co thin film by using XPS and XMCD methods at some adsorption states created by changing the coverage and temperature. Our observations by the combination of these soft x-ray surface analysis techniques (XPD, XPS, XMCD) indicate that the surface magnetic anisotropy of magnetic materials is closely connected to the chemisorbed structures of gaseous molecules.

II. EXPERIMENTS

Co thin films were prepared on a Pd(111) single crystal by the following procedure. The Pd(111) substrate was cleaned by repeated cycles of Ar^+ sputtering (2 keV) and annealing at 1000 K in an ultrahigh vacuum chamber. The cleanliness and order of the surface were confirmed by near-edge x-ray absorption fine structure (NEXAFS), low-energy electron diffraction (LEED) and XPS. Co thin films were prepared by deposition on Pd(111) with the electron-beam evaporation method at room temperature. We estimated the thickness of each film by the edge jump of NEXAFS and the Auger intensity ratio between Co *LMM* and Pd *MNN*. We prepared several Co films in the thickness of 4–6 ML, which shows a parallel magnetization when the surface is clean and a perpendicular magnetization when the surface is covered by CO at 200 K.[20,21,28]

The C 1*s* XPS, scanned-energy C 1*s* XPD and Co $L_{\mathrm{III,II}}$-edge XMCD in absorption spectra were taken at the soft x-ray grating monochromator bending-magnet station BL-7A of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF).[29] XPS and XPD measurements were performed with a hemispherical electrostatic analyzer (GAMMADATA-SCIENTA, SES-2002).[30] For high-resolution XPS measurements in the C 1*s* region, the energy of the incident x-ray was set to 430 eV and the incident angle was fixed at $\theta=30°$ above the surface, and then normally emitted photoelectron was observed. Scanned-energy XPD spectra were collected over the electron kinetic energy range of about 60–250 eV ($k_{\mathrm{c1s}}=4-8$ Å^{-1}). The available energy range was restricted by the Co *MMM* and Pd *MNN* Auger peaks. The photoelectron intensities were measured at different emission angles by rotating the crystal around both polar and azimuthal axes. Each C 1*s* intensity was normalized with the incident photon intensity. The diffraction modulation function was extracted from the intensity-energy spectra using the χ function, defined as $\chi=(I-I_0)/I_0$, where I and I_0 are the diffractive and nondiffractive intensities.[31]

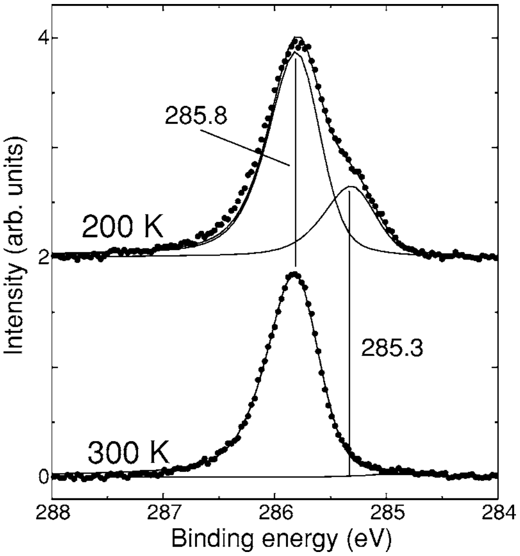

FIG. 1. C 1*s* x-ray photoelectron spectra of CO/Co(4.5 ML)/Pd(111), taken at 200 and 300 K. Peak positions are marked by vertical lines. The shoulder at 285.3 eV is only observed in the spectrum at 200 K.

For XMCD measurements, we used elliptically polarized x rays emitting downwards from the electron beam orbit in the storage ring by -0.4 ± 0.1 mrad. The degree of the circular polarization was estimated to be 0.85. The absorption spectra were recorded with the partial-electron-yield mode using a detector consisting of a 25-mm-diameter microchannel plate and two Au-coated W grids, which was placed below the sample. To enhance the surface-to-bulk ratio of the signals, the solid angle was narrowed so as to collect electrons emitted in the grazing direction. A retarding voltage (−500 eV) was applied to the second grid (closer to the MCP), while the first one was grounded. The intensity of the incident x-rays was monitored simultaneously with a Au-coated W mesh placed upstream of the sample. The XMCD spectra were obtained by reversing the magnetization of the films, while the helicity of the photon was not changed. The sample was mounted in a Helmholtz coil and was magnetized by a current pulse (~0.1 T) along the incident x rays. The remanent magnetization was examined. In order to check the magnetic easy axis of the thin film, XMCD measurements were performed at normal incidence ($\theta=90°$) for the detection of perpendicular magnetization and at grazing incidence ($\theta=30°$) for the detection of surface parallel magnetization. We measured XPS and XMCD in absorption spectroscopy in the same experiment chamber without changing the sample and detector position.

III. RESULTS

In Fig. 1, C 1*s* photoelectron spectra of CO adsorbed on Co/Pd(111) taken at 300 K and 200 K are shown. The spectrum at 300 K is well reproduced by a single Voigt function (including an asymmetry factor) located at 285.8 eV, suggesting a single site adsorption of CO. On the other hand, the spectrum taken at 200 K has an additional shoulder at

285.3 eV. This implies that there are two or more kinds of adsorption sites at 200 K. Peak shifts of photoelectron spectra of CO adsorbed on single crystal surfaces have been investigated in many systems and now it is well-understood that the C 1*s* peak of CO on the bridge or hollow site usually has a lower binding energy than that on the atop site,[23] although the peak position of bridge and hollow sites are not well-separated in many cases.

According to the previous XPS experiments for CO adsorbed on an hcp Co(0001) single crystal, the spectrum consists of a single peak when CO is adsorbed at 300 K, while two peaks are observed at 180 K.[32,33] This agrees well with our result except that the intensity of the lower binding energy peak is larger than that of the higher one in the case of a single crystal hcp Co(0001). It was assumed that CO adsorption site on Co(0001) is atop site at 300 K and atop and bridge (or hollow) sites at 180 K and below.

Note that the structure of a thin film is not always the same as that of the corresponding single crystal surface. According to a Co 2*p* photoelectron diffraction study, a Co thin film on Pd(111) has a fcc structure at least up to 20 ML.[34] Co *K*-edge extended x-ray absorption fine structure (EXAFS) study also confirmed that Co films keep a fcc structure,[35] which is different from the hcp structure in bulk Co. Although the crystal structures are different from each other, the top layer structure of fcc(111) is same as that of hcp(0001).

As described above, CO is adsorbed only at a single site at 300 K where the spin reorientation transition is not induced, while more than two sites are occupied at 200 K where the spin reorientation transition takes place. To understand the relation between adsorption fashion and magnetic anisotropy of a thin film, a detailed structure determination is necessary. The method of scanned-energy photoelectron diffraction is suitable to determine the local structural parameters of adsorbates on a surface. First, we used the projection method[36] to obtain a rough position of the C atom of CO. This method provides the locations of the nearest-neighbor backscatters by calculating a projection of the experimental modulation function onto the calculated one for all possible atomic locations relative to the emitter.

Figure 2 shows the results for CO adsorbed on Co/Pd(111) at 300 K. High intensity spots are regarded as probable positions of the nearest-neighbor substrate Co atoms. The *XZ* section ($Y=0.0$ Å) shows a unique spot at about $Z=-1.80$ Å and the *XY* section ($Z=-1.80$ Å) shows a spot at the origin. These results clearly indicate that CO is adsorbed on the atop site of the Co thin film. For a quantitative analysis, modulation functions have to be simulated. The multiple scattering calculation of diffraction (MSCD) package developed by Chen and van Hove[37] was used for the calculation. Figure 3 shows the scanned-energy photoelectron diffraction modulation functions taken at five different emission directions for the CO adsorbed on Co/Pd(111) at 300 K. The C-Co interatomic distance was determined by the *R*-factor optimization[37] to be 1.78 Å. The best-fit simulated curves for the atop site adsorption model are also plotted in the figure. They reproduce the experimental spectra well, allowing us to confirm that CO occupies only the atop site.

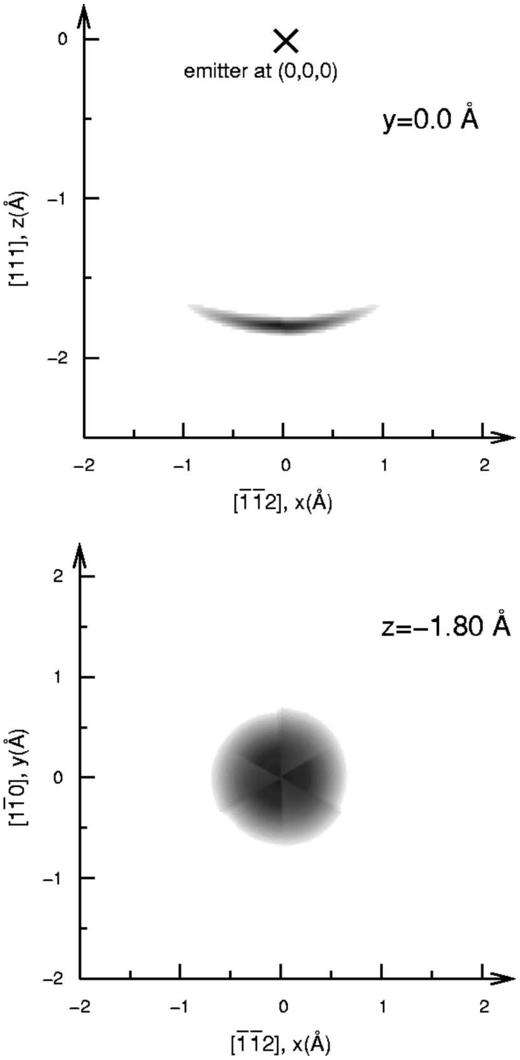

FIG. 2. Images of the nearest-neighbor Co atoms from the C emitter for CO/Co(5 ML)/Pd(111) at 300 K, obtained by the projection method. Top figure is in a section through the surface and bottom figure is in a plane parallel to the surface 1.80 Å below the C emitter.

In the case of CO adsorption at 200 K, the XPD analysis is not straightforward, since the C 1*s* spectrum at 200 K suggests a multiple-site CO adsorption as shown in Fig. 1. We used a low-resolution mode for taking the C 1*s* spectra and did not separate the two peaks for the XPD modulations because it takes a very long time to take high-resolution spectra at each photon energy and emission angle. Figure 4 shows the probability density distributions obtained by the projection method from C 1*s* XPD: the *YZ* section ($X=0.0$ Å), and two *XY* sections ($Z=-1.85$ and -1.70 Å).

The image of the *YZ* section at $X=0.0$ Å clearly indicates several adsorption sites. The image of the *XY* plane at $Z=-1.85$ Å is ascribed to the atop adsorption, while that at $Z=-1.70$ Å uniquely to the bridge site adsorption. Note that if CO were adsorbed in the hollow site, six spots should appear at the positions rotated by 30° from the observed ones.

The modulation function of the C 1*s* XPD at 200 K is shown in Fig. 5. The amplitude of the normal emission func-

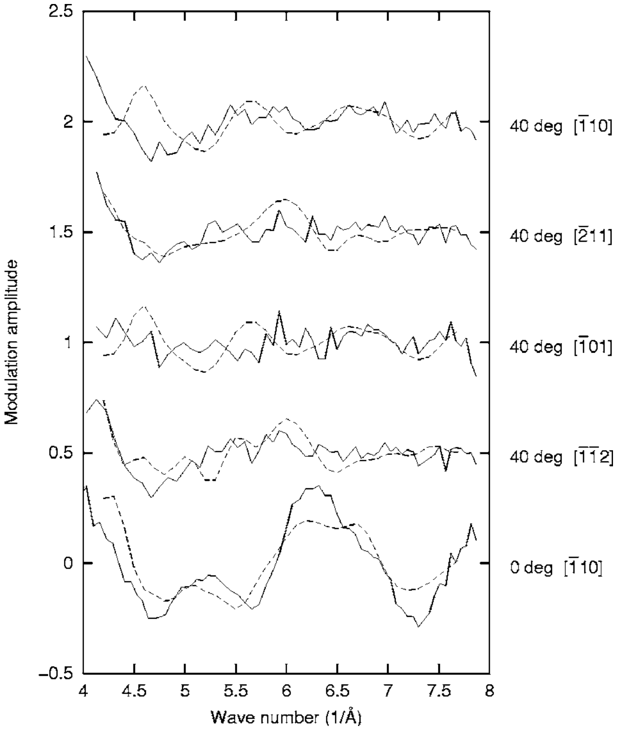

FIG. 3. Experimental (solid curves) and calculated (dashed curves) scanned-energy C 1*s* XPD modulation functions $\chi(k)$s recorded in five different emission directions for CO/Co(5 ML)/Pd(111) taken at 300 K. Denoted angles stand for the electron emission angles from the surface normal.

tion (0°) is larger than those at 40°, suggesting the dominant contribution of the atop adsorption. Compared with the function at normal emission at 300 K, the amplitude is suppressed at 200 K, although it is usually reduced at higher temperature due to thermal vibration.

From these results, we can deduce that the adsorption structure at 200 K consists of a relatively small bridge site occupation and a large fraction of atop site occupation. Calculated modulation amplitudes based on the above model at 200 K are also depicted in Fig. 5. The C-Co interatomic distances were determined by the *R*-factor optimization to be 1.83 and 2.11 Å for the atop site and the bridge site adsorption, respectively. When these interatomic distances are compared with the similar CO adsorption systems, it is recognized that the relatively long interatomic distances are obtained in this case, which indicates a relatively weak interaction between the Co thin film and the CO molecules. This trend is remarkable at 200 K as seen in the longer C-Co interatomic distance for the atop site adsorption (1.83 Å) than that at 300 K (1.78 Å). In the case of CO adsorption on a hcp Co(0001) single crystal at low temperature, the surface structure was understood by the incoherent adsorption model that all CO molecules are adsorbed on the positions slightly shifted from the high symmetry sites.[32] High CO coverage at low temperature might cause a similar adsorption structure because of the strong molecule-molecule interaction for the case of CO on Co/Pd(111), which would cause weak oscillations of the XPD spectra and poorer agreement with the simulated spectra at 200 K.

Both the XPS and XPD results clearly show that CO is adsorbed uniquely at the atop site at 300 K, while CO is adsorbed at the bridge site as well as the atop site at 200 K. Such CO adsorption behavior should have a relation to the surface magnetic behavior. To confirm this assumption, it is necessary to perform a careful experiment to observe both surface structure and magnetization in the same system and the same condition. From this standpoint, the evolutions of both C 1*s* XPS and Co $L_{\mathrm{III,II}}$-edge XMCD in absorption spectroscopy were monitored during the stepwise CO adsorption.

Figure 6 shows C 1*s* photoelectron and Co XMCD spectra from the 4.5 ML Co thin film on Pd(111) measured alternatively after each step of CO exposure at 200 K. Note that in Fig. 6, the x-ray incident angle for the XMCD measurements was set to normal so as to detect the perpendicular component of the magnetization. Before CO dosage, we confirmed that the Co thin film was fully magnetized in the surface parallel direction by the XMCD observation at grazing incidence. Thus, the nearly zero XMCD signal at low CO coverages means that the Co thin film is fully magnetized in the parallel direction. The Co film undergoes a spin reorientation transition from surface parallel to perpendicular magnetization after CO saturated adsorption.[20,21,28]

In the CO adsorption process, we define an effective exposure of 1.0 at the saturation exposure. At the early stage of CO exposure, as long as CO occupies only the atop site, Co is in-plane magnetized. At around 0.5 CO effective exposure, the shoulder at 285.3 eV starts to grow in XPS. Simultaneously, the XMCD signal gradually appears. This means that the magnetization axis begins to change from the surface parallel to perpendicular direction. At about 1.0 CO effective exposure, the intensities of both C 1*s* and Co XMCD spectra are saturated, indicating that the spin reorientation transition was completed in the entire film with saturated CO adsorption. We did not observe any further change in both photoelectron and dichroism spectra above 1.0 CO effective exposure.

Next, we studied the desorption process of the same film. As shown in Fig. 7, the shoulder at 285.3 eV of C 1*s* spectrum gradually decreases by annealing, accompanied with the disappearance of the Co XMCD, while the C 1*s* main peak intensity remains almost constant. The spin reorientation transition from the surface perpendicular to parallel magnetization is completed at 260 K, where the shoulder has disappeared in the XPS. When cooling back to 200 K, the Co XMCD does not recover its intensity and the Co thin film keeps the surface parallel magnetization. This experiment clearly shows that the spin reorientation transition due to annealing is ascribed not to a thermodynamic effect, but to a pure desorption effect of CO adsorbed on the bridge site. Although the change of the Curie temperature induced by the desorption can influence the thermodynamic parameters of the magnetic anisotropy, this effect can be neglected because the Co thin film shows nearly saturated magnetization at room temperature even at a thickness of 2 ML. Readsorption of CO at 200 K after annealing and cooling recovers the shoulder at 285.3 eV in XPS and a certain signal of XMCD. CO was adsorbed on the bridge site in this case. We have repeated these experiments for several samples of 4–6 ML Co films and found the similar behavior.

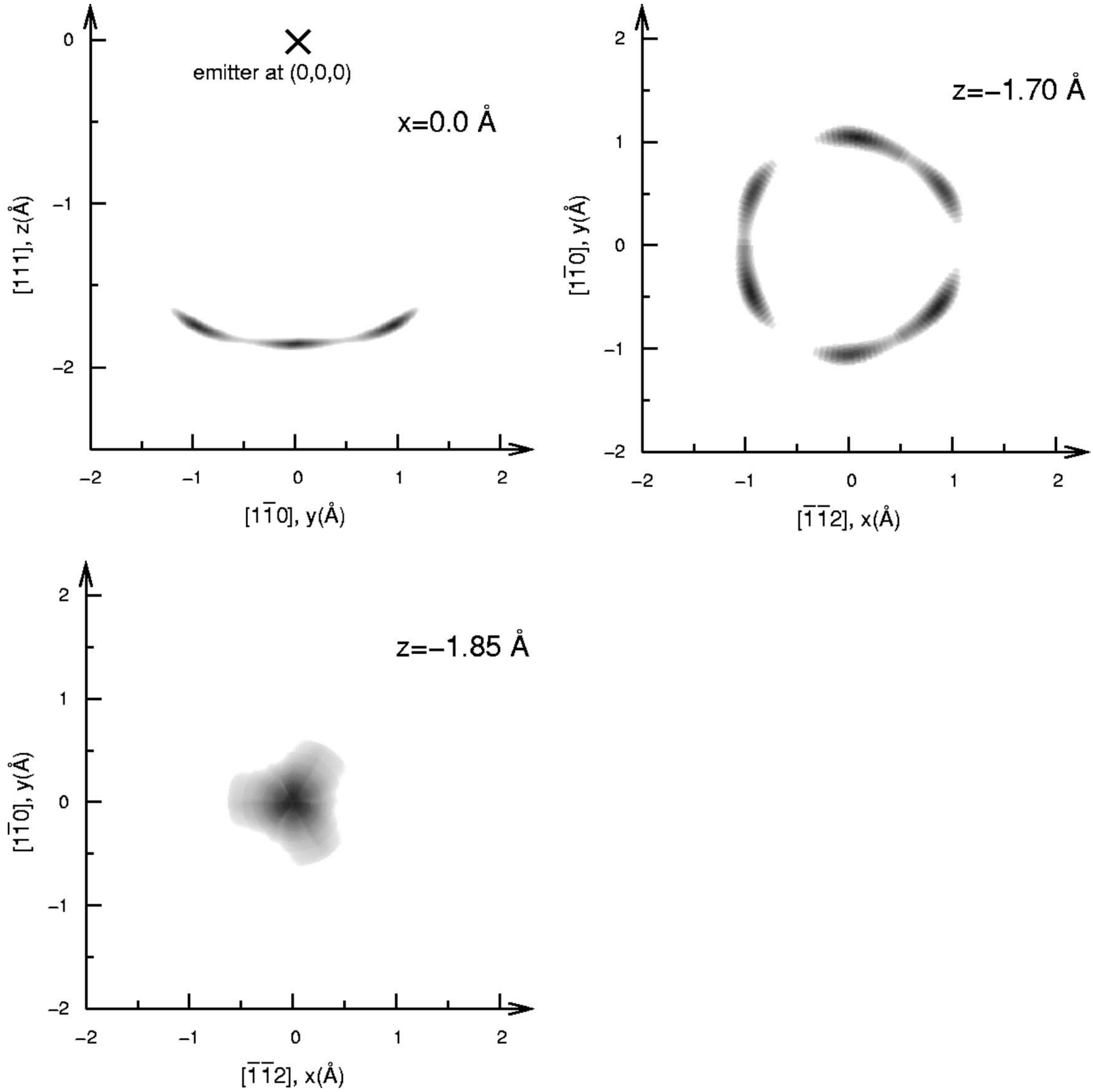

FIG. 4. Images of the nearest-neighbor Co atoms from the C emitter for CO/Co(5 ML)/Pd(111) at 200 K, obtained by the projection method. Top left figure is in a section through the surface. Bottom left and top right figures are in planes parallel to the surface 1.85 and 1.70 Å below the C emitter, respectively.

For a clearer view, the two contributions in the C 1*s* spectra are resolved by a curve fitting procedure. Figure 8 shows the intensities of the XPS peaks corresponding to both the atop and the bridge sites with the Co L_{III} XMCD peak intensity as functions of CO dosage and annealing temperature. It is realized that the spin reorientation transition is induced only by CO adsorbed on the bridge site.

Now, we can understand why the previous experiments of CO adsorption at 300 K did not detect the shift of the critical thickness of Co/Pd(111).[20,21,28] The substrate temperature was too high to adsorb CO on the energetically unfavored bridge sites. If the substrate temperature is low enough to adsorb CO on the bridge site, the surface magnetic anisotropy is drastically changed and the critical thickness shifts. It is amazing that, although the quantity of CO adsorbed on the atop site is three times as large as that on the bridge site at 200 K and the bonding between CO and Co is weaker at 200 K than at 300 K, the atop site occupation does not change the critical thickness and the bridge site occupation shifts the critical thickness by ca. 3 ML.

IV. DISCUSSION

A. Comparison with the CO adsorption on hcp(0001) Co

In the latter half of the last decade, the adsorption behavior of CO on the hcp(0001) Co single crystal surface has been revealed under several conditions.[32,33] Two stable adsorption structures have been confirmed; one is the $(\sqrt{3}\times\sqrt{3})R30°$ structure at room temperature, and the other is the $(2\sqrt{3}\times2\sqrt{3})R30°$ or $(\sqrt{12/7}\times\sqrt{12/7})R10.9°$ structure observed below 210 K.[32] An intermediate structure which corresponds to the $(\sqrt{7/3}\times\sqrt{7/3})R10.9°$ structure has also been identified below room temperature.

In the case of a Co thin film on Pd(111), LEED spots were diffused even before Co evaporation on Pd(111). After

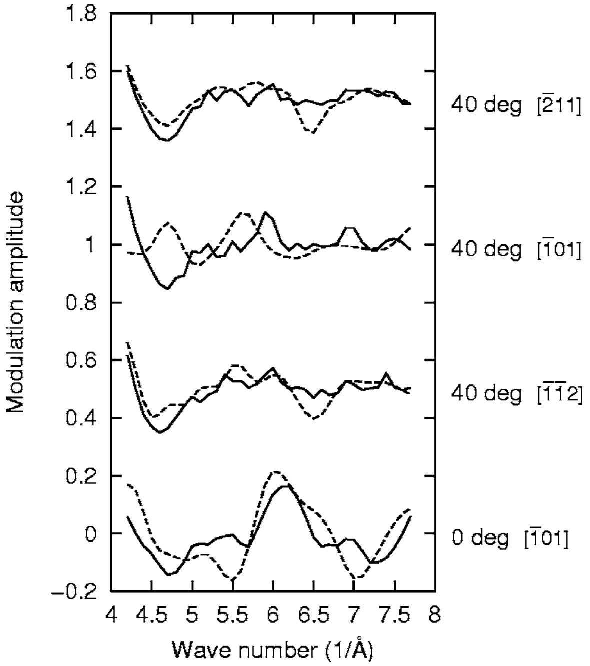

FIG. 5. Experimental (solid curves) and calculated (dashed curves) scanned-energy C 1*s* XPD modulation functions $\chi(k)$s recorded in four different emission directions for CO/Co(5 ML)/Pd(111) taken at 200 K. Denoted angles stand for the electron emission angles from the surface normal.

CO exposure, only a $(\sqrt{3}\times\sqrt{3})R30°$ pattern was observed at room temperature and no clear pattern was observed at low temperature. This is possibly because of a strong interaction between the Co thin film and the Pd substrate, as pointed out by previous experiments.[8]

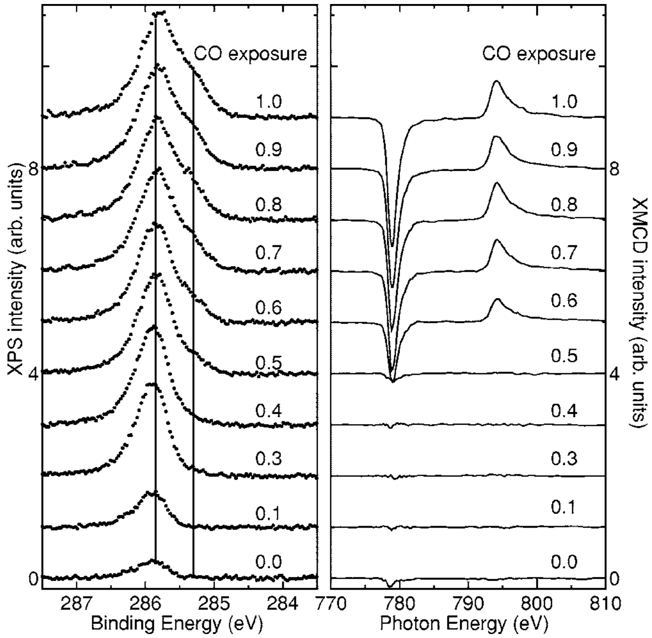

FIG. 6. C 1*s* photoelectron (left) and normal incident Co *L*-edge XMCD (right) spectra from 4.5 ML Co film on Pd(111) as a function of the CO effective exposure at 200 K.

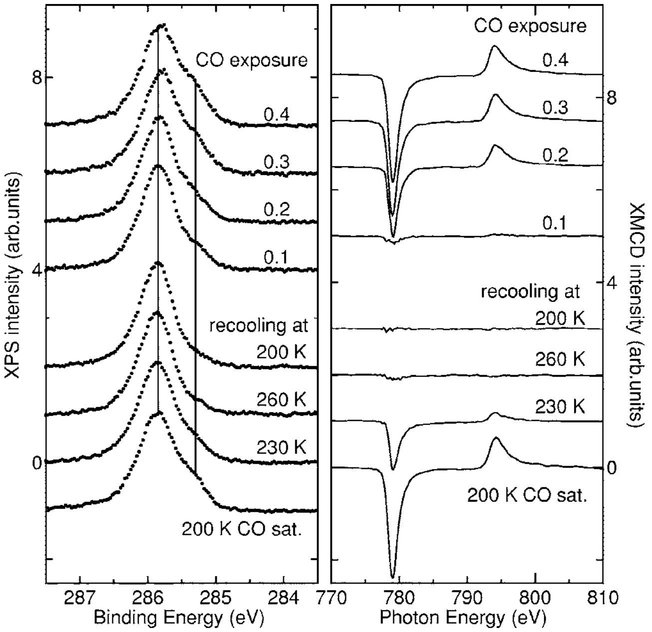

FIG. 7. C 1*s* photoelectron (left) and normal incident Co *L*-edge XMCD (right) spectra from 4.5 ML Co film on Pd(111) during heating desorption from 200 K and readsorption at 200 K.

The coverage of the saturated CO adsorption is another useful information to deduce the surface structure of CO on Co/Pd(111). The saturated coverages of CO on hcp Co(0001) for the $(\sqrt{3}\times\sqrt{3})$ structure and for the $(2\sqrt{3}\times2\sqrt{3})$ structure amount to 0.33 and 0.58, respectively.[32] According to previous XPS experiments,[32] CO molecules adsorbed on the bridge or hollow site of Co(0001) are more populated than those on the atop site in the $(2\sqrt{3}\times2\sqrt{3})$

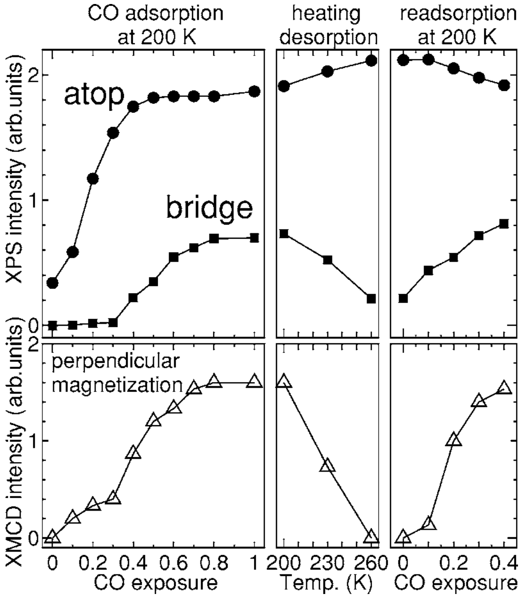

FIG. 8. C 1*s* XPS peak intensities assigned to the atop (solid circle) and bridge (solid square) sites, together with the Co L_{III} XMCD peak intensity (open triangle) for the 4.5 ML Co film on Pd(111) during step by step CO adsorption at 200 K (left), desorption by annealing (center) and readsorption at 200 K (right).

structure, indicating that CO molecules originally adsorbed on the atop site partially move to the bridge or hollow site. In the present XPS study, the C 1*s* spectrum at 200 K is composed of the main peak ascribed to the atop adsorption and a shoulder ascribed to the bridge site adsorption with the intensity ratio of 3 to 1. Such a different adsorption behavior of the Co thin film might come from imperfection in the surface morphology and perturbation in the electronic structure, since the incoherently grown Co thin film has a fcc structure on Pd(111).[34,35] However, there is no significant difference in the CO adsorption structure between hcp Co(0001) and fcc Co(111) at 300 K. This is because CO on the atop site is less influenced by the lower layer of the Co substrate.

B. Origin of the spin reorientation transition

The spin reorientation transition has been discussed by using a phenomenological model.[8] The magnetic easy axis of the film is determined by the competition among the magnetoelastic, magnetocrystalline, and shape anisotropies. Both surface and interface magnetic anisotropies of the thin films originate in magnetoelastic and/or magnetocrystalline anisotropy at the both ends of the film.

Among many magnetic thin film systems, Ni thin films on Cu(001) have been widely studied and are known to exhibit the spin reorientation transition from surface parallel to perpendicular magnetization by H, CO and O adsorption.[17,18,38,39] It is known that the deposited Ni films on Cu(001) form a well-defined layer-by-layer structure and the Ni-Ni interatomic distance is elongated to match with the Cu(001) substrate, which makes the perpendicular magnetization favorable due to the magnetoelastic anisotropy. The top layer however favors the in-plane magnetization due to the magnetocrystalline anisotropy. The energy balance of these two competing anisotropies results in the in-plane magnetization for a Ni bare film of 7–10 ML thickness. However, the CO adsorption drastically quenches the top layer Ni magnetization,[40] and causes the spin reorientation transition to the out-of-plane magnetization. Since CO is adsorbed at the atop site on a Ni(001) at 300 K,[26] it is very likely that CO is also adsorbed at the atop site on a Ni film on Cu(001). Such an atop adsorption causes the spin reorientation transition, which is in clear contrast with the present Co/Pd(111).

To understand the origin of the spin reorientation transition of the Co/Pd(111) film, we should at first consider how the magnetic moment of the top Co layer changes upon CO adsorption. The previous experiment shows that the magnetic moment of the Co film does not change its value drastically by the CO adsorption, at least in the perpendicular magnetization region.[20] Since the measurements were performed in a surface sensitive condition, it seems that the magnetic moment of the top Co layer is not reduced upon CO adsorption. Although some reduction in the magnetic moment was observed for the films with in-plane magnetization, one cannot attribute it to the reduction in the magnetic moment itself, since the remanent magnetization was investigated. Accordingly, the chemisorption-driven spin reorientation transition of Co/Pd(111) is not attributed to the reduction in the magnetic moment of the top layer, which results in the reduction in the shape anisotropy. Such a difference between Co and Ni is probably due to the much larger exchange energy of Co compared with Ni.

Next we consider the magnetoelastic and magnetocrystalline anisotropies. In contrast to the Ni films, Co films retain bulk lattice spacing indifferent of the Pd substrate.[35] Although the strong interface magnetocrystalline anisotropy favors the out-of-plane magnetization,[12] the bare Co/Pd(111) exhibits the in-plane magnetization above 3.5 ML thickness. For the multilayer Co/Pd(111) systems, the critical thickness has been reported to be about 9 ML.[8] If the magnetic anisotropy of the Co film is mainly originated at the surface or the interface, one can estimate the surface magnetocrystalline anisotropy (K_{2s}) from the critical thickness of the bare Co/Pd(111) and the multilayer system. By using the reported interface magnetocrystalline anisotropy, $K_{2i}=-300\ \mu\mathrm{eV/atom}$ (Ref. 8), K_{2s} is estimated to be $-67\ \mu\mathrm{eV/atom}$. On the other hand, since the critical thickness of CO/Co/Pd(111) is 6.5 ML at low temperature, K_{2s} for the CO adsorbed film is similarly estimated to be $133\ \mu\mathrm{eV/atom}$. Thus, the bridge site CO adsorption changes K_{2s} by $+200\ \mu\mathrm{eV/atom}$. By applying Bruno's relationship,[41] this shift corresponds to a change of $0.57\mu_{\mathrm{B}}/\mathrm{atom}$ in the orbital magnetic moment difference between surface perpendicular and parallel directions. This is consistent with the orbital moment change observed in the previous experiment,[20] although the spectra were recorded in the remanent magnetization. Above expression indicates that the bridge site adsorption of CO drastically changes the surface magnetic anisotropy of Co thin film.

It is intriguing to consider why the simple atop adsorption does not, while atop and bridge sites adsorption does induce the spin reorientation transition. One possible explanation is as follows. CO adsorption on the atop site gives little effect on the Co surface geometry, while it is likely that CO adsorbed in the bridge site pushes the bonding Co atoms away and elongates the in-plane interatomic Co distance, which in turn compresses the neighboring Co-Co atomic distances. Such structural change might enhance the out-of-plane anisotropy of the top layer. Of course, we cannot exclude other possibilities such that CO saturated adsorption plays a key role for the structural change, which favors the out-of-plane magnetization. Co *K*-edge EXAFS experiments have been tried, but they did not provide any evidence of the surface structural change.[35]

Several theoretical calculations have been reported for the effects of adsorption on a magnetic material. Pick and Dreyssé calculated the orbital magnetic moments for CO adsorbed a Co cluster and showed that the magnetization changes depending on the adsorption sites.[42] Recent calculations on the surface magnetic anisotropy of Co(0001) indicate that the CO adsorption induces the spin reorientation transition.[43] However, in the calculation, only atop site adsorption was considered. It is still unclear how the different site adsorption affects the magnetic anisotropy. Our data shows experimentally that adsorbate species on magnetic thin film influences the surface magnetic anisotropy in a different way, depending on the surface adsorption site.

C. Transition process of spin reorientation

Let us consider the process of the spin reorientation transition from surface parallel to perpendicular magnetization and vice versa. In the case of Fe/Cu(001), the domain growth was observed in the process of the temperature-driven spin reorientation transition by the secondary electron microscope with polarization analysis.[4] A mixed phase including both parallel and perpendicular magnetization domains appears in the transition process. Similar domain nucleation and two coexisting metastable spin configurations were found by using Kerr microscopy.[44] On the other hand, in the case of Ni/Cu(001), a stable canted magnetization was observed near the critical thickness.[45] Continuous rotation of the magnetic easy axis was described, including the fourth-order magnetic anisotropy constant.[45] In the case of fcc Co(111) or hcp Co(0001) thin films, some experiments showed that there is a phase composed of both parallel and perpendicular domains coexisting in the middle of the spin reorientation transition.[8] We also investigated the mixture region at about 6.5 ML thickness of Co film on Pd(111), where the Co film has an almost fully saturated magnetization along either parallel or perpendicular direction, depending on the applied magnetic field. However, other study indicated that there is a stable canted magnetic orientation around the critical thickness.[46] It seems that the magnetic phase of the Co thin film at a boundary of the transition is still under the discussion.

What is the microscopic behavior of chemisorption-driven spin reorientation transition of Co/Pd(111)? If the surface adsorption is locally connected to the surface magnetic domains, CO adsorption on a bridge site immediately causes the rotation of a spin around the CO molecule. Bridge-adsorbed CO islands must be accompanied with the PMA domains. Such a process reminds us of the spin reorientation transition proceeding with the increase of small PMA domains. XPS indicates that CO adsorbed on bridge sites amounts to about one tenth of the surface Co atoms. It means that one CO on bridge site is responsible for the spin reorientation transition of ten Co surface atoms. A microscopic study would be necessary to confirm the correlation between the molecular adsorption and the growth of the magnetic domain of the thin film.

V. CONCLUSION

We have researched precise mechanism of the chemisorption-driven spin reorientation transition of Co/Pd(111) magnetic thin films using XPS, XPD, and XMCD. This work provides a deep insight for the relation between surface adsorption structure and magnetic anisotropy of a thin film. Surface structure of CO adsorbed on Co/Pd(111) at 300 K is found to occupy the atop site, while CO occupies the bridge site as well as the atop site at 200 K with relatively long C-Co interatomic distances. We found that the spin reorientation transition of Co/Pd(111) induced by CO chemisorption occurs exclusively by CO adsorbed on the bridge site. It is confirmed that the surface magnetic anisotropy can be influenced by surface adsorption structure. These results open a new fundamental research field bridging surface chemistry and surface magnetism.

ACKNOWLEDGMENTS

This study was supported by the Grant-in-Aid for scientific research (Grant No. 14204069) and The 21st Century COE Program from the Ministry of Education, Culture, Sports, Science and Technology. One of the authors (D.M.) also acknowledges the financial support of the Japan Society for Promotion of Science for Young Scientists. The present work has been performed under the approval of the Photon Factory Program Advisory Committee (PF-PAC No. 2001S2-003).

---

*Present address: Kansai Photon Science Institute, Japan Atomic Energy Agency, Sayo, Sayo-gun, Hyogo 679-5148, Japan.

†Electronic address: ohta@chem.s.u-tokyo.ac.jp

[1] C. Chappert, D. Renard, P. Beauvillain, J. P. Renard, and J. Seiden, J. Magn. Magn. Mater. **54-57**, 795 (1986).

[2] B. N. Engel, M. H. Wiedmann, R. A. V. Leeuwen, and C. M. Falco, J. Appl. Phys. **73**, 6192 (1993).

[3] C. Liu, E. R. Moog, and S. D. Bader, Phys. Rev. Lett. **60**, 2422 (1988).

[4] J. Thomassen, F. May, B. Feldmann, M. Wuttig, and H. Ibach, Phys. Rev. Lett. **69**, 3831 (1992).

[5] W. L. O'Brien and B. P. Tonner, Phys. Rev. B **49**, 15370 (1994).

[6] D. Weller, Y. Wu, J. Stöhr, M. G. Samant, B. D. Hermsmeier, and C. Chappert, Phys. Rev. B **49**, 12888 (1994).

[7] B. N. Engel, M. H. Wiedmann, R. A. V. Leeuwen, and C. M. Falco, J. Magn. Magn. Mater. **126**, 532 (1993).

[8] S. T. Purcell, M. T. Johnson, N. W. E. McGee, J. J. de Vries, W. B. Zeper, and W. Hoving, J. Appl. Phys. **73**, 1360 (1993).

[9] Y. Wu, J. Stöhr, B. D. Hermsmeier, M. G. Samant, and D. Weller, Phys. Rev. Lett. **69**, 2307 (1992).

[10] H. A. Dürr, S. S. Dhesi, E. Dudzik, D. Knabben, G. van der Laan, J. B. Goedkoop, and F. U. Hillebrecht, Phys. Rev. B **59**, R701 (1999).

[11] C. J. Tatnall, J. P. Schille, P. J. Grundy, and D. G. Lord, J. Magn. Magn. Mater. **165**, 391 (1997).

[12] S.-K. Kim and J. B. Kortright, Phys. Rev. Lett. **86**, 1347 (2001).

[13] S.-J. Oh, W. Kim, W. Kim, B.-H. Choi, J.-Y. Kim, H. Koh, H.-J. Kim, and J.-H. Park, Appl. Surf. Sci. **169-170**, 127 (2001).

[14] O. Robach, C. Quiros, P. Steadman, K. F. Peters, E. Lundgren, J. Alvarez, H. Isern, and S. Ferrer, Phys. Rev. B **65**, 054423 (2002).

[15] S. Hope, E. Gu, B. Choi, and J. A. C. Bland, Phys. Rev. Lett. **80**, 1750 (1998).

[16] H. J. Elmers, J. Hauschild, and U. Gradmann, J. Magn. Magn. Mater. **198-199**, 222 (1999).

[17] R. Vollmer, T. Gutjahr-Löser, J. Kirschner, S. van Dijken, and B. Poelsema, Phys. Rev. B **60**, 6277 (1999).

[18] S. van Dijken, R. Vollmer, B. Poelsema, and J. Kirschner, J.

Magn. Magn. Mater. **210**, 316 (2000).

[19] R. Vollmer and J. Kirschner, Phys. Rev. B **61**, 4146 (2000).

[20] D. Matsumura, T. Yokoyama, K. Amemiya, S. Kitagawa, and T. Ohta, Phys. Rev. B **66**, 024402 (2002).

[21] T. Yokoyama, D. Matsumura, K. Amemiya, S. Kitagawa, N. Suzuki, and T. Ohta, J. Phys.: Condens. Matter **15**, S537 (2003).

[22] H. Tillborg, A. Nilsson, N. Mårtensson, and J. N. Andersen, Phys. Rev. B **47**, 1699 (1993).

[23] G. Held, J. Schuler, W. Sklarek, and H. P. Steinrück, Surf. Sci. **398**, 154 (1998).

[24] A. Föhlisch, M. Nyberg, J. Hasselström, O. Karis, L. G. M. Pettersson, and A. Nilsson, Phys. Rev. Lett. **85**, 3309 (2000).

[25] S. Terada, T. Yokoyama, Y. Okamoto, M. Kiguchi, Y. Kitajima, and T. Ohta, Surf. Sci. **442**, 141 (1999).

[26] J. T. Hoeft, M. Polcik, D. I. Sayago, M. Kittel, R. Terborg, R. L. Toomes, J. Robinson, D. P. Woodruff, M. Pascal, G. Nisbet, and C. L. A. Lamont, Surf. Sci. **540**, 441 (2003).

[27] T. Gießel, O. Schaff, C. J. Hirschmugl, V. Fernandez, K.-M. Schindler, A. Theobald, S. Bao, R. Lindsay, W. Berndt, A. M. Bradshaw, C. Baddeley, A. F. Lee, R. M. Lambert, and D. P. Woodruff, Surf. Sci. **406**, 90 (1998).

[28] D. Matsumura, T. Yokoyama, K. Amemiya, S. Kitagawa, and T. Ohta, Phys. Scr. **T115**, 583 (2005).

[29] K. Amemiya, H. Kondoh, T. Yokoyama, and T. Ohta, J. Electron Spectrosc. Relat. Phenom. **124**, 151 (2002).

[30] H. Kondoh, M. Iwasaki, T. Shimada, K. Amemiya, T. Yokoyama, T. Ohta, M. Shimomura, and S. Kono, Phys. Rev. Lett. **90**, 066102 (2003).

[31] D. P. Woodruff and A. M. Bradshaw, Rep. Prog. Phys. **57**, 1024 (1994).

[32] J. Lahtinen, J. Vaari, and K. Kauraala, Surf. Sci. **418**, 502 (1998).

[33] G. F. Cabeza, P. Légaré, and N. J. Castellani, Surf. Sci. **465**, 286 (2000).

[34] A. Atrei, G. Rovida, M. Torrini, U. Bardi, M. Gleeson, and C. J. Barnes, Surf. Sci. **372**, 91 (1997).

[35] J. Miyawaki, D. Matsumura, A. Nojima, T. Yokoyama, and T. Ohta (unpublished).

[36] P. Hofmann and K.-M. Schindler, Phys. Rev. B **47**, 13941 (1993).

[37] Y. Chen and M. A. van Hove, MSCD package, Lawrence Berkeley National Laboratory, 1998.

[38] J. Lindner, P. Poulopoulos, R. Nüuthel, E. Kosubek, H. Wende, and K. Baberschke, Surf. Sci. **523**, L65 (2003).

[39] J. Hong, R. Q. Wu, J. Lindner, E. Kosubek, and K. Baberschke, Phys. Rev. Lett. **92**, 147202 (2004).

[40] K. Amemiya, E. Sakai, D. Matsumura, H. Abe, T. Ohta, and T. Yokoyama, Phys. Rev. B **71**, 214420 (2005).

[41] P. Bruno, Phys. Rev. B **39**, R865 (1989).

[42] Š. Pick and H. Dreyssé, Phys. Rev. B **59**, 4195 (1999).

[43] Š. Pick, Solid State Commun. **127**, 531 (2003).

[44] E. Mentz, A. Bauer, T. Günther, and G. Kaindl, Phys. Rev. B **60**, 7379 (1999).

[45] B. Schulz and K. Baberschke, Phys. Rev. B **50**, 13467 (1994).

[46] J. W. Lee, J. R. Jeong, S. C. Shin, J. Kim, and S. K. Kim, Phys. Rev. B **66**, 172409 (2002).