Relationship between morphology and magnetic behavior for Gd thin films on W(110)

E. D. Tober and R. X. Ynzunza
Department of Physics, University of California at Davis, Davis, California 95616
and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkley, California 94720

C. Westphal*
Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

C. S. Fadley
Department of Physics, University of California at Davis, Davis, California 95616
and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 21 September 1995)

We have used scanning-tunneling microscopy to study the structure of Gd thin films grown on W(110) and its relationship to the magnetic properties. The film morphology is examined for different coverages and for two different post-deposition annealing temperatures (530 and 710 K), permitting predictions of the in-plane demagnetization factor and the Curie temperature that are in excellent agreement with prior ac magnetic-susceptibility measurements. The first monolayer of Gd is also found to grow in a (7×14) lateral superstructure, giving rise to in-plane lattice distortions of $\sim1\%$ as compared to the values of bulk Gd.

Over the last ten years, a number of studies of the magnetic properties of thin films of Gd grown epitaxially on W(110) single-crystal substrates has been performed.[1–12] This system of a $4f$ ferromagnetic metal deposited on a nonmagnetic transition metal has provided much interesting data, including, for example, indications of an elevated surface Curie temperature.[1,2] Although particular growth modes and film morphologies for this system have been inferred indirectly from techniques such as Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED),[1,13] no direct observations of surface morphology using scanning-tunneling microscopy (STM) have been made. In this paper, we study the effects of coverage and annealing temperature on the morphology of such Gd films with STM. These results yield a more quantitative understanding of the structure-magnetism relationships for this prototypical epitaxial ferromagnet and also reveal a new superstructure for the first monolayer.

Some important prior observations for Gd/W(110) are as follows. Weller *et al.*[1] proposed based upon AES measurements that Gd films deposited on W(110) substrates held at between 723 and 773 K grow via the Stranski-Krastanov (SK) mode [three-dimensional (3D) island growth on top of one or more epitaxial monolayers]. This same work used spin-polarized LEED and the magneto-optic Kerr effect (MOKE) to determine that the surface Curie temperature (T_{Cs}) was higher than that of the bulk (T_{Cb}) by 22 K. A later study by Tang *et al.*[2] employed spin-polarized secondary electron emission spectroscopy and spin-polarized photoelectron spectroscopy and concluded that T_{Cs} was 60 K higher than T_{Cb}, that there was a ferromagnetic alignment of the in-plane component of the surface and bulk moments, and that the surface magnetization appeared to be canted. Gd is thus one of only two ferromagnetic materials for which T_{Cs} has been observed to be greater than T_{Cb}, with the other being Tb(001), as studied by Rau *et al.* using electron capture by deuterons[14] Kolaczkiewicz *et al.*[13] further investigated the growth modes and surface structures of Gd/W(110) utilizing LEED and AES. From breaks in AES intensities as a function of coverage, Θ, they inferred that, for lower coverages [$\Theta<3$ monolayers (ML)] and when deposited at room temperature, Gd grows in the Frank–Van der Merwe (FM) mode (smooth, layer-by-layer growth) to form Gd(001). From these same data, it was suggested that the first Gd monolayer is a hexagonal (001) plane compressed by 4.4% from the bulk spacing, with the Gd[100] direction (which points along the in-plane nearest-neighbor direction) parallel to the W[001] direction. Farle *et al.* also performed a detailed study of the effects of annealing temperature and coverage on the ac magnetic susceptibility χ_{ac} (Refs. 3,4) and MOKE (Ref. 5) of this system. They found that, for films deposited at 300 K in the thickness range of 5–11 ML, annealing at 530 K after deposition sharpened and intensified the peak in χ_{ac} at T_C considerably. However, as the annealing temperature was increased to temperatures in the range of 550–710 K, the peak broadened, moved to a higher T_C, and decreased markedly in intensity. The explanation put forth for these results was that the smooth films achieved after 530 K annealing broke up into large 3D islands with increased annealing temperature.

In particular, Farle *et al.* studied the effect of postdeposition annealing on the χ_{ac} of Gd films with a total coverage of 11 ML. They observed a broad peak in χ_{ac} for these films as deposited at 300 K, which they took to be indicative of local strain and film inhomogeneity that in turn lead to a broadening in the distribution of T_C. They then annealed these 11 ML films to 530 K, which greatly sharpened and intensified the peak in χ_{ac}; this peak appeared at a T_C value of 247 K, which is only about 50 K below T_{Cb} for bulk Gd. These results are summarized in Fig. 1(d). This sharpening was thought to be due to some sort of relaxation of local strain and the formation of a more uniform and flat film. Finally, after 710 K annealing, the intensity of the peak in χ_{ac} dropped to only 4% of its original value and its position shifted to a T_C value of 283 K, which is much closer to the bulk value of 297 K [again, see Fig. 1(d)]. Farle *et al.* ex-

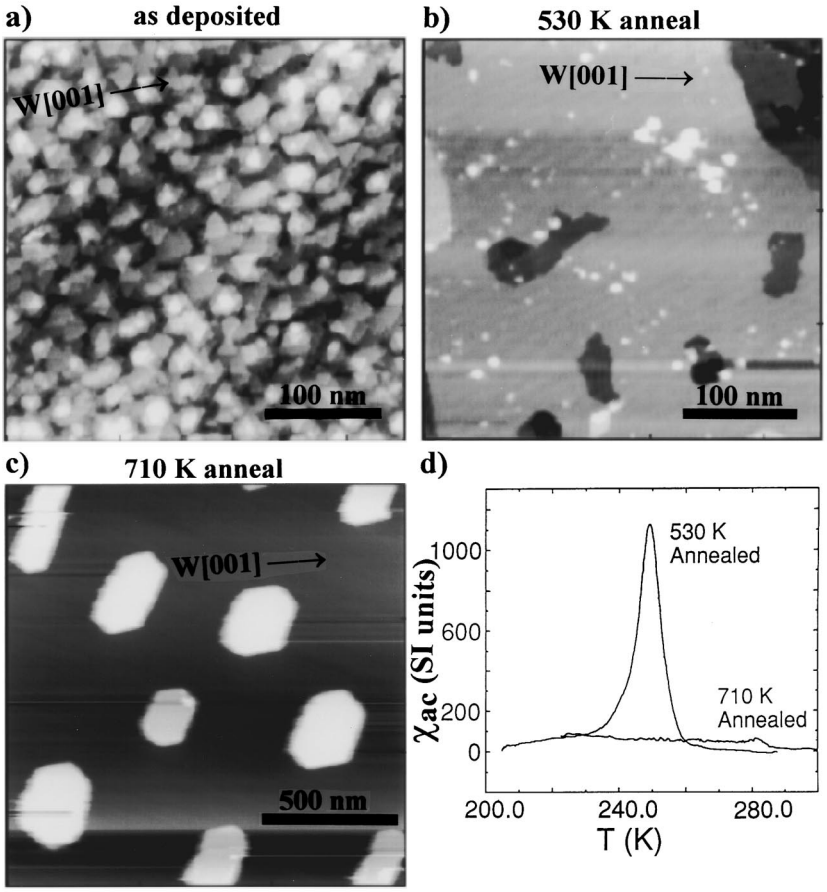

FIG. 1. Constant-current STM images of 11 ML Gd films deposited on W(110) at 300 K, with overall image size, sample bias V_b, and tunneling current I indicated: (a) film as deposited 350 nm×350 nm, $V_b=800$ mV, $I=2.00$ nA; (b) film annealed at 530 K; 350 nm×350 nm, $V_b=800$ mV, $I=2.00$ nA; (c) film annealed at 710 K; 1500 nm×1500 nm, $V_b=800$ mV, $I=1.00$ nA; (d) previously obtained ac magnetic susceptibility data for 11 ML Gd films at the same two annealing temperatures (from Ref. 4).

plained the decrease in peak intensity as arising from the formation of large three-dimensional islands with considerable open space between them, with the island shape then leading to an increase in the in-plane demagnetization factor N. This island formation, they predicted would have the effect of lowering the measured $\chi_{\rm ac}$ signal according to the relation

$$\chi_{\rm ext}=\frac{\chi_{\rm int}}{[1+N_{\chi_{\rm int}}]}, \tag{1}$$

where $\chi_{\rm ext}$ is the predicted ac susceptibility and $\chi_{\rm int}$ is the intrinsic ac susceptibility of the material.[6] From the observed increase in T_C, they estimated the average thickness of the islands that formed to be 20–25 ML. Aspelmeier *et al.*[7] then successfully modeled these results for an 11-ML-thick film annealed at 710 K by assuming circular 3D Gd islands of uniform size (7.6 nm or about 22 ML in thickness and 500 nm in diameter).

We have thus studied the surface morphology of Gd/W(110) with STM and LEED for a range of coverages from 1 to 20 ML (with special attention to 11 ML), examining the films as deposited at ambient temperature, and with final annealing at 530 and 710 K, and relating the morphology to these prior studies. All measurements were carried out in an ultrahigh-vacuum system combining LEED, Auger, and STM, which is described elsewhere.[15] The Gd films were grown at a rate of 0.11–0.15 ML/min (as determined by both a quartz crystal thickness monitor and quantitative AES measurements) at pressures of $4–5\times10^{-11}$ torr. Subsequent measurements with LEED, AES, and STM were performed at pressures of $2–3\times10^{-11}$ torr. The substrate was a tungsten single crystal, mechanically and electrochemically polished to within 0.5° of (110) as measured by x-ray diffraction. The crystal was cleaned by flashing to 2200 K, prolonged annealing at 1500–1550 K in O_2 at 5.0×10^{-7} torr, and then by flashing off the resulting oxide layer at 1825 K for 50 sec. The resulting substrate and deposited Gd films were determined to be clean by AES (<0.05 ML of combined C and O contamination), and they accumulated <0.10 ML in combined C and O after the approximately 8 h required to finish each series of LEED and STM measurements. STM images of the clean W surface showed flat terraces between monatomic steps with an average width of approximately 36 nm. The annealing temperatures of the Gd films were measured with an infrared pyrometer calibrated with a Pt-Rh thermocouple for $T<1273$ K and a W-Re thermocouple for higher temperatures. All of the AES, LEED, and STM measurements were performed at room temperature.

We first consider the effects of annealing on 11 ML films and attempt to directly correlate surface morphology with prior susceptibility measurements. STM images of an unannealed 11-ML-thick Gd film and 11 ML films annealed to 530 and 710 K for 10 min are shown in Figs. 1(a)–1(c), respectively, with accompanying single-line STM height profiles shown in Figs. 2(a)–2(c). Before annealing [Figs. 1(a), 2(a)], the film is rough, consisting of multiple-tiered structures and crevices. The LEED pattern for this surface shows a diffuse, hexagonal (1×1) pattern, indicating a poorly ordered Gd(001) film that is fully consistent with the STM image. After annealing to 530 K in [Figs. 1(b), 2(b)], the film

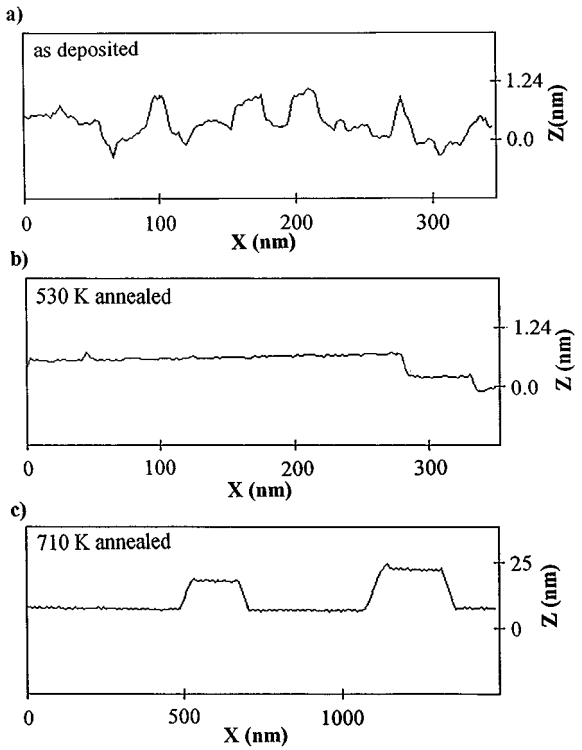

FIG. 2. Single-line STM scans of relative tip height (Z) vs horizontal tip position (X) taken from Figs. 1(a)–1(c) (scanning from left to right, parallel to the bottom of the image frames) for 11 ML Gd films deposited on W(110): (a) film as deposited [from Fig. 1(a)], (b) film annealed at 530 K [from Fig. 1(b)], (c) film annealed at 710 K [from Fig. 1(c)]. [Note that tip heights shown are approximate and are derived by comparing the observed monatomic step heights on the Gd(001) surface to the expected step height of 0.29 nm.]

covers the surface smoothly within the typical 1500 nm $\times$1500 nm STM scan; there are only a few single-atom steps of $\sim$0.3–0.4 nm in height between adjacent smooth layers and a few small mounds on the topmost layer. LEED here shows a sharp hexagonal (1×1) pattern that one would expect for a well-ordered Gd(001) film. This type of temperature-induced smoothening has been seen previously for the homoepitaxial growth of Fe thin films on Fe(001).[16] If a film prepared as in Fig. 1(a) or 1(b) is annealed to 710 K, it is found to break up into large 3D islands, which in turn sit on top of a full-coverage base monolayer of Gd [Figs. 1(c), 2(c)]; the properties of this base monolayer (including the LEED pattern) will be described in greater detail below. The Gd islands in Fig. 1(c) are further found to facet into quasi-hexagonal shapes, with one set of two shorter parallel sides lying along the [001] axis of the W substrate (which is in turn parallel to the Gd [100] direction). These islands are also of a fairly narrow size distribution, with an average area of $\sim 8.40\pm1.40\times10^4$ nm^2 and a thickness range of 11.3 ± 4.7 nm (equivalent to 23–55 ML). Roughly 32% of the film surface is covered by islands with an island density of approximately 4.1×10^{-6} per nm^2. The measured angles between the facets of these islands are $120\pm2°$, consistent with the hexagonal structure of the Gd lattice perpendicular to its [001] direction. For reference, a similar sort of island growth has been observed for Pt films deposited on W(110) and W(111) and annealed to $T>880$ K (Ref. 17) and for Ag thin films deposited on Si(110) (Ref. 18).

In order to relate these structures to magnetic properties, we first approximate these islands as thin circular disks of average thickness $t=11.3$ nm and average diameter $d=2\times[(8.40\times10^4\ \text{nm}^2)/\pi]^{1/2}=3.27\times10^2$ nm. This yields a ratio $g\equiv t/d=3.46\times10^{-2}$, from which the in-plane demagnetization factor can be calculated:[4]

$$N=\frac{\pi g}{4}-g^2. \tag{2}$$

The quantitative analysis of our STM images thus leads to a value for N of $2.6\pm0.7\times10^{-2}$, which is close to, but over twice as large as, the value of 1.0×10^{-2} estimated recently by Aspelmeier *et al.* with assumed size parameters for the islands.[6] We further note that χ_{ac} as measured after the 530 K anneal is approximately equal to χ_{int} since the film is atomically smooth and N for this case is estimated to be only about 5×10^{-7}.[4] At the peak in Fig. 1(d), the χ_{ac} signal for the 530 K annealed surface is roughly 1200 SI units. Using this value, together with the value for N determined from our STM measurements, we can use Eq. (2) to predict that the peak in χ_{ac} should drop by 97% after 710 K annealing, in excellent agreement with the 96% drop observed by Farle *et al.*[4] Furthermore, one can estimate from the previously measured thickness dependence of T_c for Gd films prepared so as to be smooth[4] that the T_c for such large flat islands of 11.3 nm thickness will be approximately 286 K, again in excellent agreement with the χ_{ac} results for the 11 ML film.[4]

Finally, we turn to another intriguing feature of the growth of Gd on W(110), which has been characterized in this study: The first monolayer of Gd forms a lateral two-dimensional superstructure of large-scale periodicity with respect to the substrate, as shown in Fig. 3. This Gd superstructure is evident in real-space constant-height STM images of a 1 ML Gd film annealed to 710 K [Fig. 3(a)] *and* of the regions between the large islands of a 11 ML Gd film annealed to 710 K [Fig. 3(c)]. It is also obvious in the reciprocal-space LEED pattern [Fig. 3(b)] for the surface in Fig. 3(a), which shows finely spaced satellite spots around the Gd and W(1×1) spots; here, the Gd(1×1) pattern coincides with the six most intense spots, as indicated by crosses in the figure. (A similar LEED pattern was observed for 1 ML coverage in Ref. 13, but with no quantitative comments as to origin.) This same structure is visible in STM between the Gd islands for *all* coverages in the range of $1<\Theta<20$ ML for films annealed at 710 K and in the range of $1<\Theta<7$ ML for films annealed at 530 K (greater coverages gave smooth multilayer films when annealed to 530 K). We find that the superstructure has rectangular periodicities along the [001] and the [$\bar{1}$10] directions of the W substrate of 23.5 ± 1.7 and 15.9 ± 1.8 Å, respectively, from STM measurements and 23.7 ± 2.1 and 16.4 ± 0.7 Å from LEED [assuming that the W(1×1) spots—indicated by circles—represent bulk distances]. These periodicities are thus very close to (7×7) with respect to W(110), which would yield 22.1 and 15.6 Å along the [001] and [$\bar{1}$10] directions. The height corrugation measured by STM is approximately 0.5 Å.

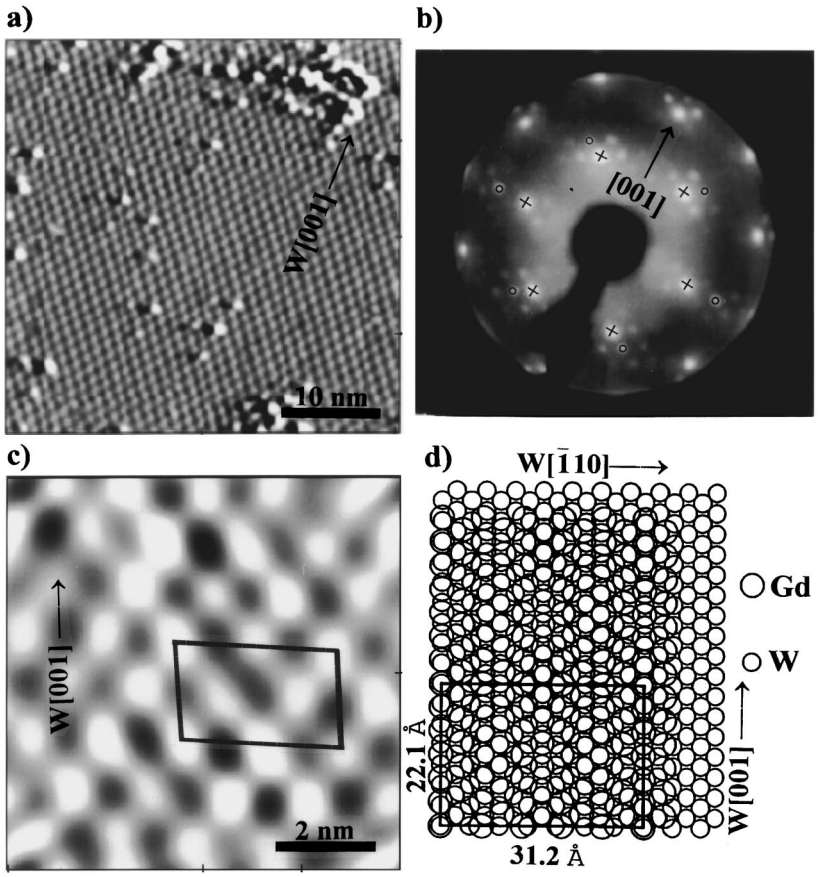

FIG. 3. (a) Constant-height STM image of the superstructure present with 1 ML of Gd annealed to 710 K: 40 nm$\times$40 nm, $V_b=800$ mV, $I=2.00$ nA. (b) LEED pattern produced by the structure in (a) at a beam energy of 102.1 eV; Gd(1×1) spots are indicated by + and $W(1\times1)$ by $\bigcirc$. (c) Constant-current STM image of the superstructure visible between the Gd islands of an 11-ML-thick film annealed to 710 K: 8 nm$\times$8 nm, $V_b=800$ mV, $I=2.00$ nA. (Thermal drift in the STM causes a slight canting of the image.) (d) Our proposed atomic model for the superstructure formed by 1 ML Gd on W(110), with the rectangular (7×14) unit cell indicated and the pseudo-(7×7) periodicity also evident.

Our suggested model for this superstructure simply overlays a slightly distorted hexagonal Gd(001) monolayer on top of the W(110) surface with the Gd [100] direction parallel to W [001] (similar to the Nishiyama-Wasserman orientation as previously suggested by Tian *et al.*[19]). As shown in Fig. 3(d), the overlayer forms a Moiré pattern with the substrate that has an overall (7×14) periodicity as judged with respect to W(110). Relative to bulk Gd, the Gd monolayer is expanded by 1.2% along the $\underline{\text{W}}$ [001] direction and compressed by 0.6% along the $[\bar{1}10]$ direction. This gives a Gd:W coincidence-lattice match of 6:7 and 5:7 along the W [001] and $[\bar{1}10]$, respectively. The corrugation is then due to variations in interplay spacing between the Gd overlayer and the W substrate over the many different Gd absorption sites involved and/or changes in the surface density of states over the unit cell. Figure 3(d) also indicates that this model has pseudo-(7×7) periodicity: Two pseudo-(7×7) cells of 22.1 and 15.6 Å along the W [001] and $[\bar{1}10]$ directions are contained in a true (7×14) cell, with the (7×7) periodicity being in excellent agreement with our STM and LEED results, as noted above. No other combinations of compression and expansion of the Gd lattice of such small extents were found to produce a superstructure with the correct periodicity. Hence these findings are in disagreement with the 4.4% compression determined for the first Gd monolayer by a previous quantitative AES study.[13] We note that somewhat similar superstructures have been observed for 1 ML of FeO grown epitaxially on Pt(111) (Refs. 20,21) and for 4 ML of Cu grown epitaxially on Ru(0001) (Ref. 22), which have been attributed to the lattice mismatch between the substrate and a weakly interacting overlayer, giving rise to a periodic rippling of the surface.

In conclusion, our STM measurements on the morphology of Gd films on W(110) prepared with and without annealing have provided a quantitative structural explanation for previously measured magnetic properties and revealed a new two-dimensional structure for the first monolayer. As deposited at room temperature, Gd does not grow layer by layer, but rather in a multilayer mode. Annealing films thicker than 7 ML at 530 K produces smooth, monatomically stepped surfaces. However, further annealing these films to 710 K causes the Gd film to break up into large 3D islands with quasihexagonal symmetry and relatively uniform size resting on a base monolayer; this is thus an example of Stranski-Krastanov growth. Careful measurement of the island dimensions for an 11 ML film enables the prediction of a 97% reduction in peak intensity for ac magnetic susceptibility (compared to 96% from prior experiments[4]) and of a Curie temperature of approximately 286 K (again in agreement with prior experiments[4]). Finally, the first monolayer of Gd is observed to form a (7×14) superstructure with pseudo-(7×7) symmetry and that is consistent with a minimally distorted hexagonal two-dimensional Gd(001) film.

The authors would like to thank D. Weller for the loan of a Gd deposition source and for many helpful comments, A. P. Kaduwela for aid in superstructure modeling, and I. Tidswell for assisting with W single-crystal alignment. This work was supported by the Office of Naval Research (Contract No. N00014-94-0162) and the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences Division (Contract No. DOE-AC03-76SF00098).

*Present address: Department of Physics, University-GHS-Essen, D-45141 Essen, Germany.

[1] D. Weller, S. F. Alvarado, W. Gudat, K. Schroder, and M. Campagna, Phys. Rev. Lett. **54**, 1555 (1985).

[2] H. Tang, D. Weller, T. G. Walker, J. Scott, C. Chappert, H. Hopster, A. W. Pang, D. S. Dessau, and D. P. Pappas, Phys. Rev. Lett. **71**, 444 (1993).

[3] M. Farle, W. A. Lewis, and K. Baberschke, Appl. Phys. Lett. **62**, 2728 (1993).

[4] M. Farle, K. Baberschke, and U. Stetter, Phys. Rev. B **47**, 11 571 (1993).

[5] M. Farle and W. A. Lewis, J. Appl. Phys. **75**, 5604 (1994).

[6] U. Stetter, M. Farle, and K. Baberschke, Phys. Rev. B **45**, 503 (1992).

[7] A. Aspelmeier, F. Gerhardter, and K. Baberschke, J. Magn. Magn. Mater. **132**, 22 (1994).

[8] A. Berger, A. W. Pang, and H. Hopster, J. Magn. Magn. Mater. **137**, L1 (1994).

[9] D. Li, C. W. Hutchings, P. A. Dowben, R. Wu, C. Hwang, M. Onellion, A. B. Andrews, and J. L. Erskine, J. Appl. Phys. **70**, 6565 (1991).

[10] D. Li, J. Zhang, P. A. Dowben, and M. Onellion, Phys. Rev. B **45**, 7272 (1992).

[11] A. W. Pang, A. Berger, and H. Hopster, Phys. Rev. B **50**, 6457 (1994).

[12] B. Kim, A. B. Andrews, J. L. Erskine, K. Kim, and B. N. Harmon, Phys. Rev. Lett. **68**, 1931 (1992).

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

[14] C. Rau, C. Jin, and M. Robert, Phys. Lett. A **138**, 334 (1989).

[15] K. Higashiyama, S. K. Lewis, R. X. Ynzunza, E. D. Tober, Y. J. Kim, and C. S. Fadley, Surf. Sci. **291**, 47 (1993).

[16] J. A. Stroscio, D. T. Pierce, and R. A. Dragoset, Phys. Rev. Lett. **70**, 3615 (1993).

[17] T. E. Madey, K. J. Song, and C. Z. Dong, Surf. Sci. **247**, 175 (1991).

[18] A. Samsaver, E. S. Hirschorn, F. M. Leibsle, and T. C. Chiang, Phys. Rev. Lett. **63**, 2830 (1989).

[19] H. Li, D. Tian, J. Quinn, Y. S. Li, S. C. Wu, and F. Jona, Phys. Rev. B **45**, 3853 (1992).

[20] H. C. Galloway, J. J. Benitez, and M. Salmeron, Surf. Sci. **298**, 127 (1993).

[21] Y. J. Kim, Ph.D. thesis, University of Hawaii, 1995.

[22] C. Günther, J. Vrijmoeth, R. Q. Hwang, and R. J. Behm, Phys. Rev. Lett. **74**, 754 (1995).