Charge-density waves and strain waves in thin epitaxial Cr(001) films on Nb

P. Sonntag and P. Bödeker
Institut für Experimentalphysik, Festkörperphysik, Ruhr-Universität Bochum, 44780 Bochum, Germany

T. Thurston
Brookhaven National Laboratory, Upton, New York 11973

H. Zabel
Institut für Experimentalphysik, Festkörperphysik, Ruhr-Universität Bochum, 44780 Bochum, Germany
(Received 23 February 1995; revised manuscript received 9 May 1995)

We have investigated the magnetic structure of thin epitaxial (001)-oriented Cr films grown on a Nb buffer layer on sapphire. By means of x-ray diffraction measurements the charge density waves (CDW) and strain waves (SW) in Cr films with thicknesses between 500 and 3000 Å have been studied. The results show that there exists an orientational pinning effect at both the Cr surface and the interface between Cr and the Nb buffer layer which causes an enlargement of the CDW-SW period, and a single $\vec{q}$ domain mode having a $\vec{q}$ vector pointing perpendicular to the surface. This pinning behavior relaxes with increasing film thickness.

I. INTRODUCTION

Below the Néel temperature of 311 K the itinerant antiferromagnet chromium exhibits a spin density wave (SDW) state, in which the spin density varies sinusoidally in space. The wave vector of the modulation may point along any {001} direction in the bcc Cr lattice. In bulk Cr there exist domains with three equally occupied modes of SDW's with their wave vectors parallel to the three possible {001} directions. The period of the SDW is incommensurate with the Cr lattice and the wave vector $\vec{q}$ is determined by the nesting of the Fermi surfaces.[1]

In recent years Cr has attracted much attention as a coupling medium in magnetic superlattices, in particular in Fe/Cr (Ref. 2) and in Co/Cr (Ref. 3) superlattices. In the [001] direction the antiferromagnetic structure of Cr causes an oscillatory ferromagnetic and antiferromagnetic alignment of the adjacent ferromagnetic layers with a two-Cr-monolayer periodicity. This has been beautifully demonstrated by Unguris *et al.*[4] who grew a Cr(001) wedge on an Fe wisker covered with another Fe(001) film. Using secondary electron microscopy with polarization analysis (SEMPA) the domain structure of the top Fe film could be imaged. Whenever the Cr thickness increases by one monolayer, the Fe magnetic domain switches its orientation by 180°. Furthermore, the authors have shown that the Cr film in proximity of an Fe layer remains in the Néel state well above the bulk Néel temperature. Recent measurements of the coercive field of Fe(001) on Cr(001) by Berger and Hopster[5] seem to indicate a single $\vec{q}$ domain state in Cr in proximity with Fe, which is oriented parallel to the surface normal. The observed spin flip transition from a longitudinal to a transversal SDW at 120 K is in agreement with bulk data. All these experiments have increased the interest in the intrinsic properties of thin Cr films. How is the poly $\vec{q}$ state affected by epitaxial strains or by hybridization effects with the substrate? What is the period of the SDW as a function of film thickness, and what is the coherence length of the SDW's? In this paper we try to answer some of these questions for Cr(001) films grown on a paramagnetic Nb substrate. This is part of a more extensive work also investigating the SDW's in Cr on insulating and on magnetic substrates, which will be reported in the future.

The modulation of the antiferromagnetic spin structure by the incommensurate SDW's causes satellite reflections to occur around the Cr fundamental Bragg reflections which can easily be observed by magnetic neutron scattering.[6–9] Since we deal here with thin samples having a small scattering volume the neutron scattering intensity due to the SDW would be too small to observe using conventional neutron sources. Therefore we have to measure the magnetic structure of our samples via x-ray scattering using synchrotron radiation. With this method we observe satellite reflections with half the period of the SDW's originating from strain waves[10–12] (SW's) and from charge density waves[13–15] (CDW's) being periodic modulations of the lattice constant and the charge density in the Cr lattice, respectively. Both the SW as well as the CDW result from the SDW.

For unstrained bulk Cr measurements of the SW and the CDW have been already reported.[10,15] Reference 15 shows the coexistence of CDW's and SW's and provides a detailed discussion about the amplitudes of both modulations.

The purpose of our present study is the investigation of the magnetic properties of thin Cr films, i.e., effects that the finite film thickness, the elastic strains, and the substrate have on the properties of the SDW's in thin Cr films, especially on the population of the three possible $\vec{q}$ modes.

II. SAMPLE PREPARATION

Using the molecular-beam-epitaxy (MBE) method we have grown single-crystalline bcc Cr(001) layers on Al_2O_3 $(1\bar{1}02)$ substrates with a 500 Å thick Nb(001) buffer layer. Nb is well known for its excellent growth quality on sapphire substrates.[16] Its use as a buffer layer for the growth of Cr(110) on Al_2O_3 $(11\bar{2}0)$ was already approved by Ankner[17] following the well-established recipe for the growth of metals on sapphire substrates first published by Kwo *et al.*[18] The first successful attempts to grow Cr(001) on a Nb(001) buffer layer on Al_2O_3 $(1\bar{1}02)$ were reported by Donner *et al.*[19]

The substrates were of high crystalline quality with mosaicities between 0.002° and 0.006° and had a miscut less than 1°. The layer deposition was carried out in a Riber EVA 32 MBE machine under ultrahigh vacuum (UHV) conditions, described in more detail in Ref. 20. A description of the growth process is given in Ref. 21. A series of Cr layers with thicknesses ranging from 500 Å to 3000 Å was grown in this fashion. After the growth the samples had been taken out of the vacuum, causing the formation of an oxide layer on top of the Cr surface.

III. X-RAY MEASUREMENTS

A. Experimental methods

The structural characterization of our samples has been done with two different x-ray setups under normal atmospheric pressure conditions and at room temperature. For x-ray total reflectivity measurements and out-of-plane Bragg scattering we made use of a high-resolution triple-axis x-ray diffractometer at a conventional x-ray source with a Si(220) monochromator using Mo $K\alpha_1$ radiation. For the in-plane characterization by means of grazing incidence x-ray diffraction we used a surface diffractometer at a rotating anode generator with a Cu target. The (002) reflection of a highly oriented pyrolitic graphite monochromator was used to select the Cu $K\alpha$ wavelength. A detailed description of those setups and the characterization methods is given in Ref. 22.

With this equipment we were able to gain multiple structural information about our samples. The thicknesses of the different layers a sample consists of, i.e., Nb, Cr, and Cr oxide, as well as the electron densities and roughnesses of the various layers and interfaces could be determined with x-ray total reflectivity measurements.[23] Using x-ray Bragg diffraction methods in the high angle regime we could investigate the crystalline structure of the samples, i.e., the structural coherence lengths as well as the mosaicities of the layers. To gain information about the in-plane structure and the epitaxial relations between the different layers, we performed Bragg diffractometry on lattice planes perpendicular to the sample surface. For this purpose we used an x-ray beam with a glancing incident angle with respect to the surface generating an evanescent wave parallel to the surface.[24]

To investigate the magnetic structure of our samples, i.e., the CDW's and the SW's we made use of a horizontal four circle diffractometer at the X22B beam line of the National Synchrotron Light Source (NSLS) in Brookhaven. To achieve both a good resolution of $\Delta K/K \approx 8 \times 10^{-4}$ and a high beam intensity, we used Ge(111) crystals as monochromator and analyzer. The wavelength of the x-ray radiation was chosen to be $\lambda = 1.50$ Å.

For the mounting and cooling of the samples we applied a close cycle He refrigerator cryostat with Be x-ray windows.

B. X-ray scattering amplitude for CDW's and SW's

The scattering amplitude for a Cr lattice, which exhibits both CDW's and SW's, can be calculated as follows. The SW and the CDW can be described as a sinusoidal modulation of the atomic position vector $\vec{r}_j$ and the total charge $\rho_j(\vec{r})$, respectively, of an atom in the Cr lattice according to

$$\vec{r}_j = \vec{r}_j^{\,0} + \vec{\Delta}\sin(2\vec{q}\cdot\vec{r}_j^{\,0}) \,, \tag{1}$$

$$\rho_j(\vec{r}) = \rho^0(\vec{r}) + \sigma(\vec{r})\cos(2\vec{q}\cdot\vec{r}_j^{\,0}), \tag{2}$$

where $\vec{\Delta}$, $\vec{q}$, $\vec{r}_j^{\,0}$, $\rho^0(\vec{r})$, and $\sigma(\vec{r})$ are, respectively, the displacement amplitude parallel to $\vec{q}$, the wave vector of the SDW, a position vector of the jth atom in the paramagnetic state, the form factor of Cr without the CDW, and the amplitude of the charge modulation.

Thus the x-ray scattering intensity in a longitudinal scan around a fundamental Cr Bragg reflection at $\vec{K} = \vec{\tau}$ can be calculated as[15]

$$\begin{aligned} I = {} & |\rho^0(\vec{K})|^2\delta(\vec{K}-\vec{\tau}) \\ & + \frac{1}{4}|\rho^0(\vec{K})\vec{K}\cdot\vec{\Delta} + \sigma(\vec{K})|^2\delta(\vec{K}+2\vec{q}-\vec{\tau}) \\ & + \frac{1}{4}|\rho^0(\vec{K})\vec{K}\cdot\vec{\Delta} - \sigma(\vec{K})|^2\delta(\vec{K}-2\vec{q}-\vec{\tau}), \end{aligned} \tag{3}$$

where $\vec{\tau}$ is a reciprocal lattice vector in the paramagnetic state, and $\rho^0(\vec{K})$ and $\sigma(\vec{K})$, respectively, are the Fourier transforms of $\rho^0(\vec{r})$ and $\sigma(\vec{r})$.

Equation (3) yields the intensity for two satellite reflections at $\vec{K} = \vec{\tau} \pm 2\vec{q}$ and the fundamental Bragg reflection at $\vec{K} = \vec{\tau}$.

Figure 1 displays the positions of the satellite reflections in the reciprocal space. Since most of the satellite intensity results from the SW's,[15] there are only satellites observable which have a $\vec{q}$ component pointing along the direction of the scattering vector $\vec{K}$ belonging to the fundamental Cr Bragg reflection. Any other $\vec{q}$ modes lead to satellite intensities that are almost zero, since the scattering amplitude of the SW's is proportional to $\vec{K}\cdot\vec{\Delta}$, where $\vec{\Delta}$ is parallel to $\vec{q}$.

In the following we show results from scans around the [002] and the [011] Bragg reflections of our (001) oriented Cr films, including the adjacent satellite reflections. The scans have been peformed along all three {001} directions around both fundamental Bragg peaks. To determine the phase transition and the Néel temperature, we measured the satellite reflections over a temperature range from 13 K to 310 K.

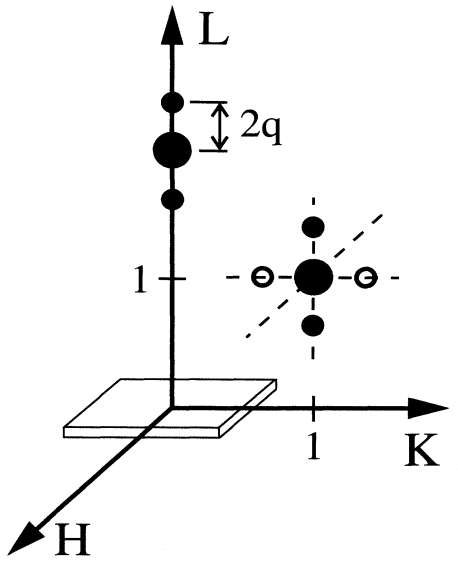

FIG. 1. The positions of the SW satellite reflections (small circles) around the Cr[002] and the Cr[011] Bragg reflections (large circles) in the reciprocal space. The open circles design the in-plane satellites which we did not observe in our Cr films on Nb.

IV. RESULTS

A. Structural characterization

The structural characterization of five samples with thicknesses ranging from 500 Å to 3000 Å yielded multiple information about the growth quality of our Cr(001) films on Nb/sapphire. First, via small angle reflectivity measurements the samples could be determined to consist of three layers with different electron densities and roughnesses σ_j. Above the substrate having a roughness of approximately 2 Å there is a 500 Å thick Nb buffer layer with approximately 4 Å roughness followed by a Cr layer with $\sigma_{Cr} \approx 5$–10 Å. A 15–20 Å thick top layer of Cr oxide having almost the same roughness as the Cr covers the layer structure and prevents further oxidation. The thickness of the oxide layer is in good agreement with *in situ* oxidation studies of Cr(110) by Stierle *et al.*[25] Investigating the crystalline structure of the Cr layers we measured the in-plane and out-of-plane coherence lengths to be $L_{\|}^0 = 100$–300 Å and $L_{\perp}^0 = 0.3D - 0.65D$, respectively, where D is the film thickness. The mosaicities of the Cr films could be determined to be $\Delta\Theta_{\perp} = 0.3°$–$0.6°$ and $\Delta\Theta_{\|} = 0.5°$–$0.9°$. With in- and out-of-plane measurements a single domain Cr lattice could be observed. All those measurements show that our samples exhibit a high single crystalline quality.

B. Magnetic structure

Figure 2 shows typical satellite reflections situated on the shoulders of the fundamental Cr[002] Bragg reflection of a 3000 Å thick Cr film on Nb/sapphire and at a temperature of 20 K.

From the width of the satellite reflections the coherence length of the out-of-plane CDW's and SW's could be deduced to be approx. 60% of the structural coherence length in the out-of-plane direction for all our samples.

Additionally we have determined the period of the modulation which is shown in Fig. 3 as a function of D. The modulation period P is enlarged for all films, where the bulk value $P_0 = 29.5$ Å is being approached with increasing thickness following a typical relaxation behavior according to

$$P = \frac{\gamma}{D} \ln\left(\frac{D}{P_0}\right). \tag{4}$$

Here γ is a fit parameter which we determined to be 903 Å^2. Equation (4) is usually used to describe the structural relaxation of strained epitaxial films on a substrate.[26] In that case P and P_0 would be the lattice constant of the strained film and the unstrained bulk material, respectively.

Furthermore, we investigated the temperature dependence of the position and the intensity of the satellite reflections.

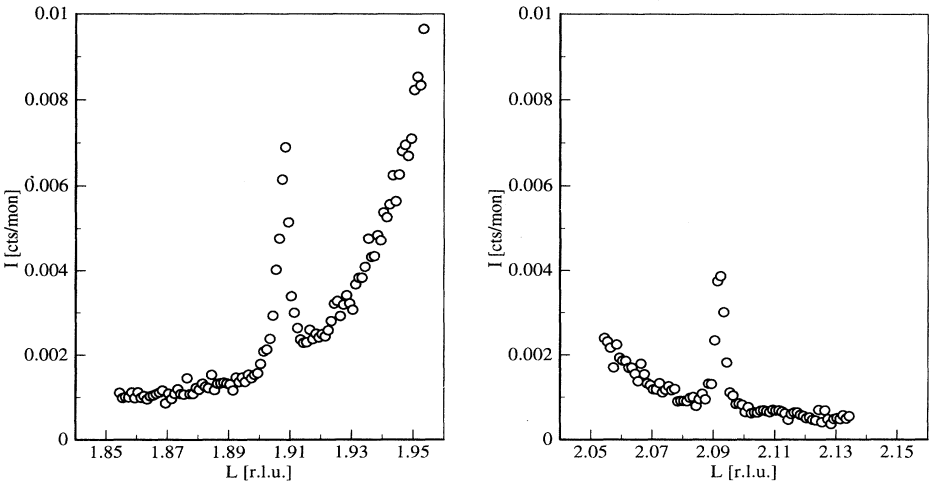

FIG. 2. Satellite reflections on both sides of the Cr[002] reflection of a 3000 Å thick Cr film on Nb/sapphire at a temperature of T=20 K.

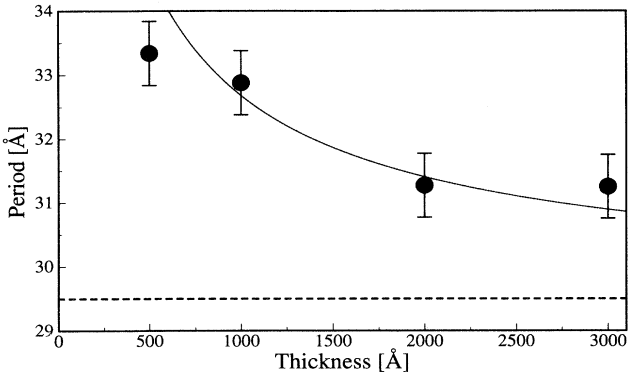

FIG. 3. The period of the out-of-plane CDW and SW as it depends on the Cr layer thickness D. The dotted line designs a relaxation curve fitted to the data. The dashed line denotes the bulk value of 29.5 Å.

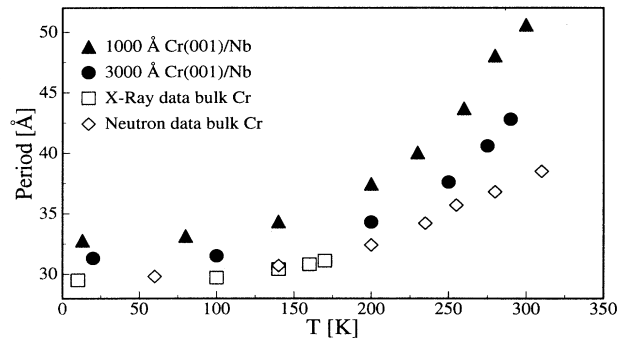

FIG. 4. The temperature dependence of the CDW-SW period of a 3000 Å thick Cr film on Nb and a 1000 Å thick Cr film compared with the results of bulk Cr measurements. The bulk data are taken from Refs. 9 and 11.

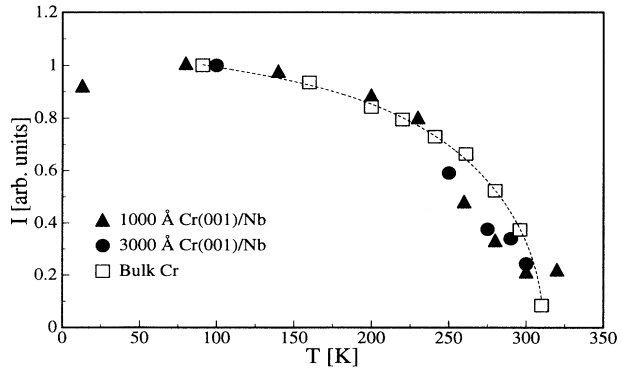

FIG. 5. The temperature dependence of the CDW-SW satellite intensity of a 3000 Å thick Cr film on Nb and a 1000 Å thick Cr film compared to the bulk behavior measured by means of x-ray diffraction (Ref. 27). The dotted line is a guide to the eye designing the bulk behavior. The intensity is normalized to 1 at T=100 K.

Figure 4 displays the CDW-SW period as a function of the temperature for two Cr films with thicknesses of 1000 Å and 3000 Å compared with bulk measurements done by means of neutron and x-ray scattering.[9,11] The deviation of the CDW/SW period observed in the Cr films from the bulk value increases with increasing temperature. This effect appears to be much stronger in the 1000 Å thick film. The temperature dependence of the satellite intensity is shown in Fig. 5 as compared with bulk measurements.[27] Over a wide temperature range below $T \approx 200$ K the behavior of the thin film data is the same as for bulk Cr. At 250 K a sudden drop of the satellite intensity is observed in the thin films. The Néel temperature seems to be reduced compared to bulk Cr and the Néel transition is smeared out. This could be explained as an effect of epitaxial strains, as suggested by Werner *et al.*[9]

Next we studied the satellite reflections around the Cr[011] fundamental peak. This position in reciprocal space is particularly interesting since here both in- and out-of-plane components of the CDW's and SW's can be investigated. In Fig. 1 the respective scans parallel to the K direction (in-plane component) and L direction (out-of-plane component) are reproduced. The experiments show that no satellite reflections belonging to a $\vec{q}$ vector pointing along an in-plane direction could be observed. Therefore we have to conclude that the SDW is strongly polarized along the [001] growth direction.

A comparison between out-of-plane and in-plane measurements performed around a Cr[011] reflection is provided in Fig. 6.

V. DISCUSSION

From recent neutron and x-ray studies on the SDW's in bulk Cr we know that there exists an orientational surface pinning effect which suppresses the in-plane SDW modes.[27] Hill *et al.* performed both x-ray and neutron diffraction experiments on Cr bulk crystals with an (001) oriented surface. Looking at the SDW's with neutron scattering their samples seemed to be in a poly-$\vec{q}$ mode in which all possible SDW modes were equally populated. Using x-ray scattering around an off-axis Cr Bragg reflection and comparing the results with theoretical calculations for a poly-$\vec{q}$ state the out-of-plane mode appears to be stronger than those having $\vec{q}$ vectors parallel to the surface plane. This behavior could be explained by a surface pinning effect suppressing the in-plane SDW's and leading to a nearly single $\vec{q}$ domain state when observed with x rays, since x rays only provide information about the surface of the bulk sample.

This observation suggests that the behavior of our Cr films could be a result of an orientational interface pinning effect at both the Cr oxide surface and the Cr/Nb interface. This pinning effect appears to be temperature dependent, since the observed period of the out-of-plane CDW and SW shows a strong temperature dependence. The deviation of the period from the bulk values increases with increasing temperature. As expected for an interface effect this behavior is stronger in the thinner film.

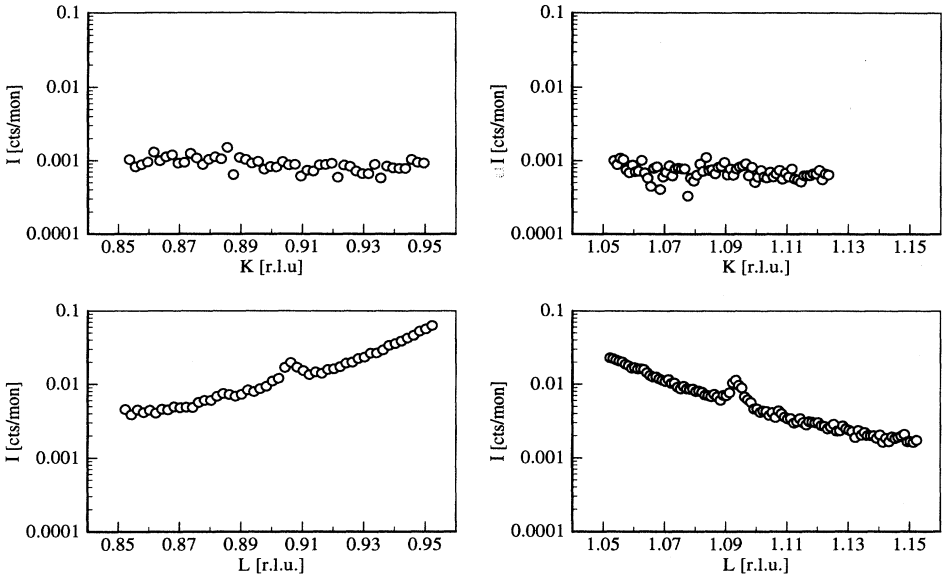

FIG. 6. Scans around the satellite reflections adjacent to the Cr[011] reflection of the same sample as mentioned in Fig. 2 taken at T =20 K. The upper part of this figure shows scans along the K direction in reciprocal space. The lower part displays scans along the L direction. It can be seen that the in-plane SW component observable via K scans is suppressed compared to the out-of-plane mode.

VI. CONCLUSIONS

Our measurements described above provide valuable information about the magnetic structure of thin Cr(001) films on Nb on sapphire. We have observed an orientational pinning effect of the CDW's and SW's depending on temperature and thickness and leading to a single $\vec{q}$ domain state with $\vec{q}$ pointing perpendicular to the film plane. Measurements of the out-of-plane SW-CDW satellite reflections show that this pinning also influences the period of the out-of-plane modulations which is enlarged compared to the bulk value. The Néel temperature of the Cr films appears to be lower than in bulk Cr, and the transition is smeared out probably due to strain effects.

ACKNOWLEDGMENTS

We wish to thank W. Oswald and J. Podschwadek for technical assistance in this study, K. Theis-Bröhl and W. Donner for sample preparation, B. Ocko for his help during the measurements at the NSLS, and D. Gibbs and J. Hill for valuable discussions. Support from the Deutsche Forschungsgemeinschaft through Grant No. SFB 166 ("Structural and magnetic phase transitions") is gratefully acknowledged, as well as the travel grant from the Volkswagen-Stiftung. The research was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical sciences (DOE Contract No. DE-AC02-76CH00016).

[1] E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).
[2] P. Grünberg, R. Schreiber, Y. Pang, M. B. Brodsky, and H. Sowers, Phys. Rev. Lett. **57**, 2442 (1986).
[3] N. Metoki, W. Donner, T. Zeidler, and H. Zabel, J. Magn. Magn. Mater. **126**, 397 (1993).
[4] J. Unguris, R. J. Celotta, and D. T. Pierce, Phys. Rev. Lett. **69**, 1125 (1992).
[5] A. Berger and H. Hopster, Phys. Rev. Lett. **73**, 193 (1994).
[6] V. N. Bykov, V. S. Golovkin, N. V. Ageev, V. A. Levdik, and S. I. Vinogradov, Dokl. Akad. Nauk. SSSR **128**, 1153 (1959) [Sov. Phys. Dokl. **4**, 1070 (1960)].
[7] L. M. Corliss, J. M. Hastings, and R. J. Weiss, Phys. Rev. Lett. **3**, 211 (1959).
[8] G. E. Bacon, Acta Crystallogr. **14**, 823 (1961).
[9] S. A. Werner, A. Arrott, and H. Kendrick, Phys. Rev. B **155**, 528 (1966).
[10] Y. Tsunoda, M. Mori, N. Kunitomi, Y. Teraoka, and J. Kanamori, Solid State Commun. **14**, 287 (1974).
[11] D. Gibbs, K. M. Mohanty, and J. Bohr, Phys. Rev. B **37**, 562 (1988).
[12] R. Pynn, W. Press, S. M. Shapiro, and S. A. Werner, Phys. Rev. B **13**, 295 (1976).
[13] S. Nakajima and Y. Kurihara, J. Phys. Soc. Jpn. **38**, 330 (1975).
[14] A. Kotani, J. Phys. Soc. Jpn. **38**, 974 (1975).
[15] M. Mori and Y. Tsunoda, J. Phys. Condens. Matter **5**, L77 (1993).
[16] S. M. Durbin, J. E. Cunningham, and C. P. Flynn, J. Phys. F **11**, L 223 (1981); **12**, L 75 (1982).
[17] J. F. Ankner, Ph.D. thesis, University of Illinois at Urbana-Champaign, 1990.
[18] J. Kwo, D. B. McWhan, M. Hong, E. M. Gyorgy, L. C. Feldman, and J. E. Cunningham, in *Layered Structures, Epitaxy, and Interfaces*, edited by J. M. Gibson and L. R. Dawson, MRS Symposia Proceedings No. 37 (Materials Research Society, Pittsburgh, 1985).
[19] W. Donner, N. Metoki, A. Abromeit, and H. Zabel, Phys. Rev. B **48**, 14745 (1993).
[20] K. Bröhl, P. Bödeker, N. Metoki, A. Stierle, and H. Zabel, J. Cryst. Growth **127**, 682 (1993).

[21] P. Sonntag, P. Bödeker, K. Bröhl, T. Thurston, and H. Zabel, Nucl. Instrum. Methods, B **97**, 468 (1995).
[22] P. Sonntag, W. Donner, N. Metoki, and H. Zabel, Phys. Rev. B **49**, 2869 (1994).
[23] H. Zabel, Appl. Phys. A **58**, 159 (1994).
[24] H. Dosch, *Critical Phenomena at Surfaces and Interfaces*, Springer Tracts in Modern Physics, Vol. 126 (Springer-Verlag, Berlin, 1992).
[25] A. Stierle, P. Bödeker, and H. Zabel, Surf. Sci. **327**, 9 (1995).
[26] W. D. Nix, Met. Trans. A **20**, 2217 (1989).
[27] J. P. Hill, G. Helgesen, and D. Gibbs, Phys. Rev. B **51**, 10 336 (1995).