Reversible H-Induced Switching of the Magnetic Easy Axis in Ni/Cu(001) Thin Films

D. Sander, W. Pan, S. Ouazi, and J. Kirschner
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle/Saale, Germany

W. Meyer, M. Krause, S. Müller, L. Hammer, and K. Heinz
Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany

(Received 22 March 2002; revised manuscript received 13 August 2004; published 10 December 2004)

A reversible switching of the easy axis of magnetization for Ni on Cu(001) from in plane to out of plane is found by changing the partial pressure of hydrogen in the gas phase around the sample, allowing even for oscillations of the magnetization direction. A quantitative low-energy electron diffraction study of the diffracted intensity versus electron energy [$I(E)$] shows that the hydrogen-induced spin reorientation transition is accompanied by changes of the tetragonal distortion of the topmost Ni layer upon hydrogen adsorption. Surprisingly, the orientation switch to perpendicular to the surface comes with a relaxation, i.e., reduction of the film's tetragonal distortion rather than its amplification.

DOI: 10.1103/PhysRevLett.93.247203 PACS numbers: 75.30.Gw, 75.70.Ak, 75.70.Cn

In general, the spontaneous magnetization in thin magnetic films is either in plane or perpendicular to the surface plane of atoms. The magnetic anisotropy energy (MAE) determines the orientation of the film magnetization. Different contributions have been identified, which modify the MAE: film thickness [1], temperature [2], composition [3], stress [4], adsorbate coverage [5], or, e.g., the presence of a small external magnetic field [6]. By varying one of these parameters the spontaneous magnetization can switch the direction and a spin reorientation transition (SRT) is observed. With increasing film thickness most frequently a shape anisotropy driven SRT from perpendicular to in plane is observed, typically at a critical thickness of the order of half a dozen monolayers. An exceptional case is a so-called "reverse SRT," i.e., a SRT from in plane to perpendicular. Because of the tetragonal distortion of the film, the most well-known example for this kind of behavior is Ni on Cu(001) [1,7,8].

This Letter reveals surprising new features for the system Ni/Cu(001) concerning the influence of hydrogen adsorption: There is a H-induced SRT [8] and we show by magnetic and crystallographic measurements complemented by gas pressure and surface coverage measurements that the hydrogen-induced reverse SRT is reversible, the reversibility of the SRT leads to an oscillatory sequence of in-plane and perpendicular magnetization when the hydrogen coverage is made to oscillate as controlled by the ambient hydrogen pressure, and the reverse SRT is accompanied by a relaxation, i.e., reduction of the film's tetragonal distortion rather than its amplification. Very likely these features bear the potential to construct a hydrogen-sensitive magnetic switch.

The magnetism related experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with magnets for *in situ* magneto-optical Kerr effect (MOKE) measurements [4]. The Cu(001) crystal was prepared by cycles of Ar ion bombardment (2 μA, 2 keV) and subsequent annealing at 800 K until no contaminations were detected by Auger electron spectroscopy and a sharp LEED pattern had developed. Ni was deposited from an high purity (99.99 + %) rod at a rate of approximately one monolayer (ML) per 150 s as controlled by a quartz thickness monitor (residual gas pressure $<3 \times 10^{-10}$ mbar). Hydrogen (99.999 + %) was then introduced via a leak valve; a quadrupole mass spectrometer recorded the purity of the gas (partial pressures p_H given below are corrected for the H sensitivity of the pressure gauge). Crystal curvature measurements were performed to monitor both the film stress during growth and the H-induced change of the surface stress of the Ni film, from which an independent estimate of the H coverage was derived. The crystallography of the film and its morphology were investigated by quantitative LEED and by scanning tunneling microscopy (STM), respectively, where the sample was in a different UHV vessel allowing for even lower residual gas pressure ($\approx 1 \times 10^{-10}$ mbar) both during Ni deposition and measurements. After deposition of eight ML Ni and cooling to about 100 K LEED intensity vs energy spectra, $I(E)$, were recorded with a computer-controlled video method [9] for the (10), (11), (20), (21), and (22) beams up to an electron energy of 600 eV (accumulated data base width: $\Delta E \approx 1800$ eV). This took 15 min so that residual gas adsorption could be kept well below 1 ML. This is mandatory to detect the H-induced structural changes upon subsequent H exposure, and to avoid spurious surface contamination by other adsorbates. Eventually, the sample was investigated by STM. An image evaluation of the nominally 8 ML film showed only three height levels with domain weights of 20%, 71%, and 9% attributed to domains of 7, 8, and 9 ML, respectively (effective film thickness 7.9 ML). This justifies to use a flat 8 ML film in the LEED analysis, in particular, as analyses of films of neighbored thicknesses showed that the multilayer relaxation is thickness independent in this coverage range.

Full dynamical calculations were applied using the matrix-inversion method for the layer diffraction and the layer-doubling method for the stacking of layers [10]. The H-covered film was treated as a composite layer, where on-top, bridge, and hollow H-adsorption sites were tested at a coverage $\theta_H = 1$ (1 H atom per surface Ni atom). Electron attenuation was considered by a constant imaginary potential ($V_{0i} = -5.0$ eV) and the real part of the inner potential, V_{0r}, was taken to be energy dependent [11]. This has been proven to be important for the correct reproduction of the crystallographic in-plane lattice parameter a_p. In an earlier LEED analysis of epitaxial Ni films on Cu(001) carried out by part of the present authors [7] a constant value of V_{0r} was used. This led to a slightly reduced value of a_p, rather than the correct value of Cu(001), $a_p = 2.550$ Å at $T \approx 100$ K, as taken from crystallographic tables and confirmed by a careful other LEED analysis considering the energy dependence, $V_{0r}(E)$ [12]. Because of the considerable reduction of the data acquisition time it was possible to keep the surface much cleaner than in the earlier work [7]. For both the clean and hydrogen covered film the first six interlayer spacings $d_{i,i+1}$ ($i = 0, 5$) were varied in steps of 0.005 Å ($d_{01} = d_H$ denotes the distance between the H and top Ni layer). Layer spacings below the fifth Ni layer were set to a constant value d_b, which was also fitted (note that the Ni-Cu interface did not need to be considered as in a depth of about 12 Å it is hidden by electron attenuation). In addition to the structural parameters also different isotropic vibration amplitudes of the top and subsurface Ni atoms were taken as fit parameters. The best fit was identified by the Pendry R factor, and error limits were estimated by its variance [13].

The main result concerning the magnetic properties is a H-induced reversible switching of the easy magnetization axis of an 8 ML thick Ni film as presented in Fig. 1. When uncovered (or for low values of p_H) this Ni film has an in-plane easy axis of magnetization. By increasing p_H from 9.3×10^{-10} to 2.7×10^{-8} mbar we detect a remanent polar MOKE signal, indicative for a perpendicular easy axis of magnetization. As indicated by the vanishing polar MOKE signal a subsequent reduction of p_H reverts the magnetization back to in plane. This switching of the magnetization orientation is fully reversible as apparent from the succession of polar MOKE signals in Fig. 1(a), and it has to be correlated with the p_H profile in Fig. 1(b).

The H coverage θ_H was calculated from the hydrogen partial pressure and the adsorption temperature of 322 K [14]. The resulting θ_H curve for the 8 ML film reveals that at $\theta_H = 0.23$ the easy axis of magnetization switches from in plane to out of plane [Fig. 1(c)]. The time dependence of the SRT in response to a change in p_H is determined by the dynamics of the H coverage on the Ni surface. As the desorption rate at 322 K is sizable, it seems that H is an ideal adsorbate for a reversible SRT. This is contrary to oxygen adsorption, which induces an irreversible SRT since the adatoms do not desorb after reduction of the O_2 pressure; see also [5]. Experiments at different Ni thicknesses indicate that H-coverage values of $\theta_H = 0.15$, 0.23, and 0.5 are sufficient to induce the SRT for 9, 8, and 7 ML Ni films, respectively.

The change of the magnetic anisotropy with p_H is recorded by applying a small magnetic field (1 mT) normal to the film surface. The magnetic response is measured by the polar MOKE signal as illustrated in Fig. 2 for 8 ML. For sufficiently small p_H a linear curve with no hysteresis is observed, which characterizes an in-plane easy axis of magnetization. The slope of this curve is inversely proportional to the magnetic anisotropy: a higher p_H induces a lower magnetic anisotropy. The rectangular hysteresis curves measured for the largest p_H value show full remanence which as such indicates an easy out-of-plane direction of the magnetization. Figure 2 suggests that the magnetic anisotropy depends on the H coverage: a larger θ_H favors an out-of-plane

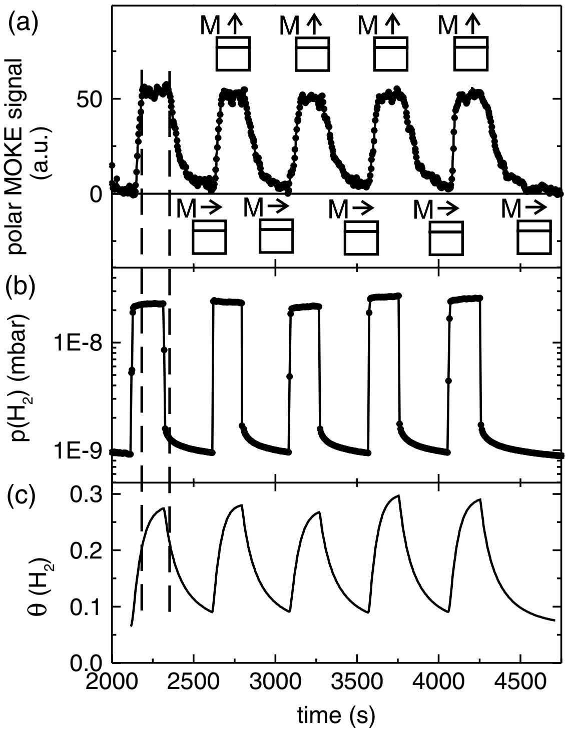

FIG. 1. (a) H-induced variation of the polar MOKE signal of an 8 ML Ni film on Cu(001) at 322 K. The switching of the easy axis of magnetization from in plane, $M\rightarrow$, to perpendicular to the Ni film, $M\uparrow$, due to a p_H variation, as displayed in panel (b), is apparent [the time delay between the signals is caused by the dynamics of the H-adsorption process (see text)]. (c) Calculated θ_H for the pressure variation of (b). The broken lines indicate that at $\theta_H = 0.23$ the magnetization direction switches from in plane to out of plane and back.

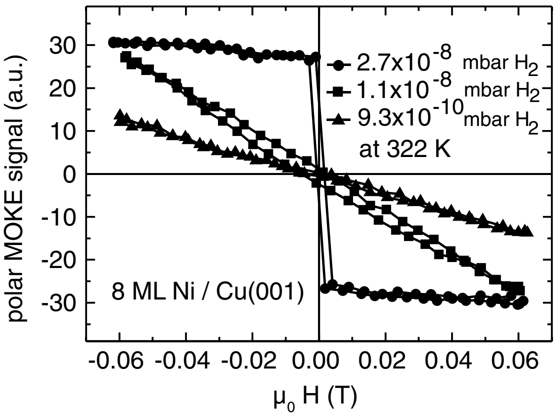

FIG. 2. Polar MOKE measurements for the Ni film of Fig. 1(a) at different H-partial pressures. The slopes of the curves at smaller $p_{\rm H}$ indicate a hard magnetization direction perpendicular to the film. The rectangular hysteresis curves obtained at large $p_{\rm H}$ identifies a perpendicular easy magnetization direction.

orientation of the magnetization. The following discussion of the H-induced structural change of the film indicates that the Ni surface layer relaxation drives this SRT.

Comparison of the experimental LEED $I(E)$ spectra for the clean and H-covered 8 ML Ni film (Fig. 3) reveals clear modifications induced by H adsorption: shifts of peaks or changes of their shape and/or height are observed. The corresponding structural changes are resolved by full dynamical intensity analyses. For the clean film an excellent $R_{\rm min}^{\rm clean} = 0.073$ results, and the corresponding structural parameters are displayed in Table I. As expected, the lateral strain [$\epsilon_\parallel = +2.5\%$, calculated using $a_p = 2.487$ Å for the (001) layers of bulk Ni at $T \approx 100$ K] of the Ni film due to pseudomorphic growth on Cu(001) leads to a vertical contraction, i.e., tetragonal distortion. This has been identified before as the driving force for the out-of-plane magnetization of thicker Ni films on Cu(001) [8]. On spatial average of the clean film ($\bar{d}^c = 1.708$ Å) the vertical contraction is $\bar{\epsilon}_\perp^c = -2.9\%$ in near-quantitative agreement with the value resulting from continuum elasticity theory [15], $\bar{\epsilon}_\perp = -2(c_{12}/c_{11})\epsilon_\parallel = -3.2\%$ (Ni: $c_{12} = 152$ GPa, $c_{11} = 249$ GPa). This tetragonal distortion gives rise to a magnetoelastic anisotropy contribution to the MAE, which is absent in cubic systems. Its magnitude is $B_1^{\rm eff}(\epsilon_\parallel - \epsilon_\perp)$ [15]. We measured the effective magnetoelastic coupling constant $B_1^{\rm eff}$ for 8 ML Ni on Cu(001) as 3.5 MJ/m^3 [16], and this result supports the view that the tetragonal distortion favors a perpendicular magnetization direction via magnetoelastic coupling. Note that the structural analysis reveals a nonuniform tetragonal distortion in the film. The top spacing $d_{12} = 1.675$ Å is contracted most, whereas the layer spacings below are identical within our error limits (± 0.01 Å), and a vertical surface layer contraction as large as $\epsilon_\perp^{c,S} = -4.8\%$ results.

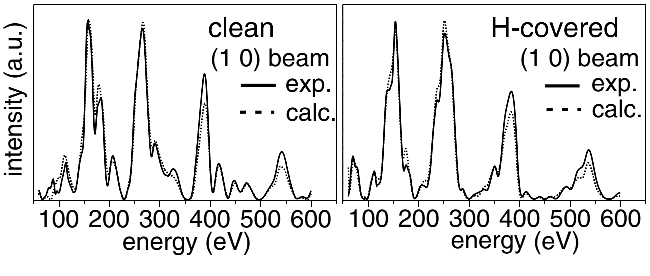

FIG. 3. LEED $I(E)$ spectra of the (10) beam for the clean 8MLNi/Cu(001) film (left) and the hydrogen covered film, H/8 ML Ni/Cu(001) (right). Continuous curves refer to experimental data, dotted curves to calculated best-fit spectra.

For the hydrogen covered 8 ML film the LEED analysis yields again an excellent best-fit quality ($R_{\rm min}^{\rm H} = 0.078$), which allows the determination of the adatom position: Hydrogen adsorbs in the fourfold hollow site with an adsorption height of $d_{\rm H} = 0.32$ Å. The latter is equivalent to a reasonable value of the hydrogen radius, $r_{\rm H} = 0.58$ Å (the other adsorption sites produce much less favorable R factors, $R_{\rm min}^{\rm H} > 0.13$, and, in addition, physically unreasonable values of $r_{\rm H}$). The adsorption height $d_{\rm H}$ agrees with a previous ion-scattering study [17], which, however, did not identify the layer relaxation induced in the Ni film. This relaxation as resulting from the present LEED analysis is summarized in the last line of Table I. The most important feature is that the topmost layer spacing d_{12} is relaxed upon H adsorption to 1.770 Å. This is a remarkable result, as the SRT of the clean Ni film is driven by the tetragonal distortion, and one might have speculated that a further H-induced compression of the layer spacing is responsible for the H-induced SRT. As is obvious, however, this is not the case. Instead, the H-induced relaxation reduces the tetragonal surface distortion, $\epsilon_\perp^{{\rm H},S} \approx 0$, but the average tetragonal distortion is only little modified ($\bar{\epsilon}_\perp^{\rm H} = -2.5\%$). Thus, a SRT driven by an H-induced enhanced magnetoelastic anisotropy is excluded.

The SRT for a bare Ni film on Cu(001) occurs at a thickness of 10–11 ML [8] and a submonolayer H coverage shifts this SRT to a lower thickness. The Ni/Cu(001) system is unique in the sense that no structural transition

TABLE I. Vertical layer spacings $d_{i,i+1}$ (Å) for the best-fit structures as retrieved by quantitative LEED. The last digit indicates the location of the R-factor minimum with respect to the 0.005 Å structural search grid. Note that the (001) layer spacing in bulk Ni is 1.759 Å.

	$d_{\rm H}$	d_{12}	d_{23}	d_{34}	d_{45}	d_{56}	$d_{\rm b}$
eight ML Ni		1.675	1.720	1.705	1.715	1.720	1.710
H/8 ML Ni	0.31	1.770	1.695	1.700	1.710	1.710	1.710

occurs at the SRT from in plane to out of plane of the clean Ni film at 11 ML thickness [8]. The tetragonal distortion, which favors the out-of-plane magnetization, is present in the film in the whole thickness range up to the end of pseudomorphic growth around 18 ML, well beyond the SRT. The in-plane magnetization of thinner Ni films comes as a surprise, and it has been ascribed to the anisotropy contribution from the interfaces, which favor in-plane magnetization [1,8]. In view of this picture, our results suggest that hydrogen adsorption reduces the magnetic surface anisotropy, and this makes the magnetoelastic anisotropy the dominant contribution to the MAE.

The essential aspect of the SRT is a balancing of different anisotropy contributions, driven by hydrogen adsorption. However, largely different energy scales describe both phenomena. Whereas the adsorption energy of hydrogen is 1 eV/atom [14], the competing magnetic anisotropy contributions are approximately 4 to 5 orders of magnitude smaller, e.g., the shape anisotropy of Ni is 12 μeV/atom [15]. In view of the small magnetic anisotropy energy, the adsorption process is a dramatic effect, and subtle details of the adsorbate-induced change of the electronic structure may determine the SRT.

Nevertheless, very general arguments illustrate that the small magnetic anisotropy of bulk cubic elements (Ni : $K_1 = -0.4\ \mu$eV/atom) can be ascribed to the quenching of the orbital moment, which is induced by the crystal field [18]. On the contrary, a partial unquenching of the orbital moment is expected for a tetragonally distorted system, and the magnetic anisotropy is enhanced. This view is corroborated by perturbation theory, which suggests that the magnitude of the anisotropy is proportional to ξ^2/W for uniaxial systems, whereas for cubic systems it is proportional to ξ^4/W^3 [ξ is the spin-orbit coupling (50–100 meV), and W is the $3d$ bandwidth (a few eV) [18]]. These values indicate that the change from a uniaxial system towards a more cubic system reduces the magnetic anisotropy by 3 orders of magnitude, and vice versa. Therefore, it seems plausible that the H-induced layer relaxation from $d_{12} = 1.675$ Å (clean Ni) to $d_{12} = 1.77$ Å (H-covered Ni) induces a corresponding reduction of the magnetic surface anisotropy, as the uniaxial distortion of the layer is reduced. We may further suggest that the large contraction ($\epsilon_{\perp}^{c,S} = -4.8\%$) of the topmost layer spacing as compared to bulk Ni might be an important aspect of the large magnetic surface anisotropy of Ni of order 100 μeV/atom [5,8].

Our results offer highly accurate structural parameters for comparison to theoretical studies which recently were performed for both structure and magnetic anisotropy of the H/Ni system [19]. The authors performed state-of-the-art *ab initio* calculations, which offer an explanation of the electronic origin of the H-induced change of the magnetic anisotropy. The calculations indicate that the strong hybridization between H and Ni leads to an outward relaxation of the topmost Ni-layer spacing, a reduction of the magnetic moment of the topmost Ni layer, and to a reduction of the magnetic surface anisotropy. The authors calculate a nontrivial structural relaxation upon H coverage, which leads to substantial outward relaxation of the topmost Ni-layer spacing (1.74 Å) and a contracted second-layer Ni spacing (1.67 Å) as compared to the inner Ni-layer spacings (1.69 Å). Our experimental results qualitatively confirm their prediction of the H-induced structural relaxation.

The proposed connection between surface relaxation and magnetic anisotropy is expected to be of general validity. This view is corroborated by a recent calculation of the O-induced change of magnetic anisotropy of a Ni stack [5]. The authors claim that a significant aspect of the change of the magnetic anisotropy upon adsorption is the O-induced lattice relaxation. These examples suggest that, irrespective of the details of the electronic interaction, the layer relaxation is a common feature of these adsorbate-driven SRTs. Highly accurate structural data are called for to unravel the interplay between adsorption, structural relaxation, and magnetic anisotropy.

In conclusion, our results provide experimental evidence for the intimate relation between surface relaxation and magnetic anisotropy. The adsorbate-induced layer relaxation of tetragonally distorted Ni films reduces the magnetic surface anisotropy, and this drives the adsorbate-induced SRT.

---

[1] B. Schulz *et al.*, Phys. Rev. B **50**, 13467 (1994).
[2] M. Farle, Rep. Prog. Phys. **61**, 755 (1998).
[3] W. Weber *et al.*, Phys. Rev. Lett. **76**, 3424 (1996).
[4] D. Sander, Rep. Prog. Phys. **62**, 809 (1999).
[5] J. Hong *et al.*, Phys. Rev. Lett. **92**, 147202 (2004).
[6] H. Oepen *et al.*, Phys. Rev. B **61**, 9506 (2000).
[7] W. Platov *et al.*, Phys. Rev. B **59**, 12641 (1999).
[8] R. Vollmer *et al.*, Phys. Rev. B **60**, 6277 (1999).
[9] K. Heinz, Rep. Prog. Phys. **58**, 637 (1995).
[10] M. A. Van Hove *et al.*, *Surface Crystallography by LEED* (Springer, New York, 1979).
[11] J. Rundgren, Phys. Rev. B **68**, 125405 (2003).
[12] S. Walter *et al.*, Surf. Sci. **458**, 155 (2000).
[13] J. B. Pendry, J. Phys. C **13**, 937 (1980).
[14] K. Christmann *et al.*, J. Chem. Phys. **60**, 4528 (1974).
[15] D. Sander, J. Phys. Condens. Matter **16**, R603 (2004).
[16] T. Gutjahr-Löser *et al.*, J. Appl. Phys. **87**, 5920 (2000).
[17] I. Stensgaard *et al.*, Phys. Rev. Lett. **54**, 711 (1985).
[18] P. Bruno, in *Magnetismus von Festkörpern und Grenzflächen, Physical Origins and Theoretical Models of Magnetic Anisotropy* (Forschungszentrum Jülich, Jülich, 1993), pp. 24.1–24.28.
[19] F. Máca *et al.*, Czech. J. Phys. **53**, 33 (2003); F. Máca *et al.*, J. Magn. Magn. Mater. **272–276**, 1194 (2004).