# Anomalous reorientation phase transition of the magnetization in fct Ni/Cu(001)

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An unusual change of direction of the magnetization ($M$) in Ni/Cu(001) monolayers from in-plane at low temperature to perpendicular at high temperature is measured by *in situ* ferromagnetic resonance and the magneto-optic Kerr effect. Two boundaries for the appearance of the perpendicular component and for the vanishing of the parallel component of the magnetization are determined as a function of temperature and film thickness. In between, stable intermediate directions of $M$ are measured. The reorientation occurs with a continuous rotation of $M$, similar to a second-order phase transition. It is shown that the temperature-dependent volume contribution to the magnetic anisotropy must be included in the interpretation of the spin reorientation transition. [S0163-1829(97)00834-5]

The spin reorientation transition (SRT) of the magnetization in ultrathin ferromagnetic films has recently attracted much interest, experimentally[1–8] as well as theoretically.[9–19] SRT describes the fact that the easy axis of the magnetization changes as a function of film thickness or temperature. One reason for the interest is that temperature driven SRT's may become of technological importance, leading to magnetic thin-film sensors or switches. From a basic research point of view, one should note that the existence of a perpendicular magnetization is nontrivial since the demagnetizing energy and the entropy of disorder[9] favors in-plane magnetization in thin films.

Many experimental studies have focused on Fe- and Co-based thin films.[1–3,5–8] It was observed that at a fixed temperature below the Curie temperature $T_c$ the magnetization changes with decreasing thickness $d$ from an in-plane to a perpendicular direction, starting below some critical thickness $d_c$. Similarly, at a certain thickness a decrease of temperature triggers the SRT at some critical (reorientation) temperature $T_r$. It is generally accepted that the SRT represents a phase transition. But the choice of the order parameter seems unclear. Three different phases[19] may exist, corresponding to one with a perpendicular magnetization $M_\perp$ only, one where an in-plane magnetization $M_\parallel$ appears (at some critical thickness $d_{c1}$ or temperature $T_{r1}$) and one where $M_\perp$ has disappeared ($d_{c2}$, $T_{r2}$). In this picture the coexistence of $M_\perp$ and $M_\parallel$ may be the result of the presence of domains with in-plane and perpendicular orientations or be due to a tilted (single-domain) magnetization. The order parameter could be $M_\perp$ or in analogy to structural phase transitions,[20] the angle of the magnetization with respect to the film plane. In both cases it vanishes above the critical temperature as it should. We will come back to this.

It should be noted that the thickness $d$ is a new but discrete variable, whereas the temperature $T$ is a ''true'' thermodynamic variable. *A priori* both are not related. In addition, heating and cooling allows a clear test for the reversibility of phase transitions. For Ni/Cu(001) we find with *increasing* temperature a reversed transition from an *in-plane* magnetized state to a *perpendicular* one; that is, the ''order parameter'' does increase with temperature. This is obviously unphysical. For such a reversed SRT the definition of an order parameter needs to be reconsidered.

In terms of the currently accepted microscopic theories[10,16,18] this behavior cannot be understood, and we will demonstrate that the temperature dependence of the surface and volume contribution ($K_2^S$,$K_2^V$) to the magnetic anisotropy energy (MAE) is all important. The temperature-dependent SRT has been modeled by a Hamiltonian including dipolar and exchange interactions, the positive $K_2^S$, favoring a perpendicular magnetization, and the entropy of disorder of the magnetization. $K_2^S$ at $T=0$ K is taken as a constant, and the temperature dependence enters through the entropy term, which favors in-plane magnetization. The volume anisotropy $K_2^V$ is not included. This is a severe limitation, and it was pointed out[21] that pseudomorphic growth of Fe, Co, and Ni on different metal substrates manipulates more $K_2^V$ than $K_2^S$. Especially in the case fct Ni/Cu(001), $K_2^V$ is large[21,22] and responsible for the unusual thickness-dependent SRT observed by many groups[21–27] at a critical thickness $d_c$. However, a temperature-dependent SRT was never reported for this system. $d_c$ is given by the balance between the intrinsic (magnetocrystalline) anisotropy $K_2 = K_2^V + 2K_2^S/d_c$ and the shape anisotropy $2\pi M^2$. Furthermore, it is well known that the MAE is temperature dependent.[21,28–30] In bulk Co and Ni reorientations of $M$ have been quantitatively described by the temperature dependence of experimentally determined second- and higher-order anisotropy constants.[30] From an experimental point of view, it seems straightforward to describe the SRT in thin films in the same way by the different temperature dependences of $K_2^S$ and $K_2^V$. In the case of Gd and Ni both $K_2^S(T)$ and $K_2^V(T)$ have been measured.[21,31,32] In the following, we will show that the anomalous SRT in Ni/Cu(001) as a function of $T$ is well understood by the temperature dependence of the MAE if $K_2^V(T)$ and higher-order anisotropy contributions ($K_4$) are included.

Face-centered-tetragonal Ni films (4–10 ML) were grown on Cu(001) at room temperature in ultrahigh vacuum, as described earlier.[22,27,33] Quantitative low-energy electron-diffraction measurements[34] and scanning tunneling microscopy studies[35] confirmed the structural homogeneity up to 11

 

ML and the nearly perfect pseudomorphic growth. Angular-dependent ferromagnetic resonance (FMR) in ultrahigh vacuum was measured *in situ* with the magnetic field rotated in the (110) plane normal to the (001) plane of the film. Hysteresis loops as a function of temperature were recorded by magneto-optic Kerr effect (MOKE) in the polar geometry. As observed earlier[2,3] the study of the SRT is experimentally difficult, if measurements are performed in zero magnetic field. The magnetization tends to break up into domains masking a possible tilted orientation. The best studies are the ones where single-domain properties are recorded like in our FMR investigation.

For a complete and relevant analysis the FMR data are evaluated in terms of the free-energy density for a tetragonal system including second- and fourth-order contributions and the Zeeman energy:

$$E = -\vec{H}\vec{M} + 2\pi M^2\cos^2\theta - K_2\cos^2\theta - \frac{1}{2}K_{4\perp}\cos^4\theta - \frac{1}{2}K_{4\parallel}\frac{1}{4}(3+\cos 4\varphi)\sin^4\theta. \quad (1)$$

$\varphi$ is the angle of $M$ with respect to the [100] direction in the film $(x,y)$ plane and $\theta$ between $M$ and the $z$ axis (film normal). $K_2$, $K_{4\perp}$, and $K_{4\parallel}$ are the second- and fourth-order terms of the MAE. For cubic symmetry one has $K_2 = 0, K_{4\perp} = K_{4\parallel}$ (denoted as $K_1$ in some literature). As discussed in detail elsewhere,[27] the balance between the different parameters $K_i$ determines the out-of-plane $\theta_{\mathrm{eq}}$ and the in-plane angle $\varphi_{\mathrm{eq}}$ of the magnetization:

$$\sin^2\theta_{\mathrm{eq}} = \frac{K_2 + K_{4\perp} - 2\pi M^2}{K_{4\perp} + \frac{1}{4}(3+\cos 4\varphi_{\mathrm{eq}})K_{4\parallel}}. \quad (2)$$

From the angular dependence of the ferromagnetic resonance field $H_R$ one determines all anisotropy parameters with high precision in a standard way.[22,27]

In Fig. 1 we show $H_R$ $(\theta_H)$ for a 7.5 ML film at four different temperatures. The minimum of $H_R$ which is a measure of the easy magnetization axis shifts from $\theta_H = 90°$ (in-plane) at 90 K to $\theta_H = 0°$ (perpendicular) at 332 K. Hence, it is evident that $M$ has switched from a parallel state at 90 K [Fig. 1(a)] to a perpendicular orientation at 332 K [Fig. 1(d)] contradicting the entropy argument. In addition, Figs. 1(b) and 1(c) show that intermediate stable angles do exist at 150 and 300 K. To obtain the equilibrium angles of $M$ in zero magnetic field,[27] we simulated[22,27,28] the angular dependence $H_R$ (solid lines) and determined the $K_i$ of Eq. (1). The resulting $\theta_{\mathrm{eq}}$ [Eq. (2)] of the spontaneous magnetization is indicated in Figs. 1(b) and 1(c). These FMR data provide unambiguous experimental evidence that indeed there is a *monotonic* temperature-dependent SRT from an in-plane to a perpendicular direction with *increasing* temperature. The temperature interval for the continuous rotation is more than 200 K. We will come back to this later.

The unusual SRT is confirmed by polar Kerr effect experiments for an 8.2 ML film. In Fig. 2 we show *in situ* hysteresis loops with the magnetic field applied normal to the film plane. The shape of the loops changes gradually from a typical hard-axis loop at low temperature to a square loop at

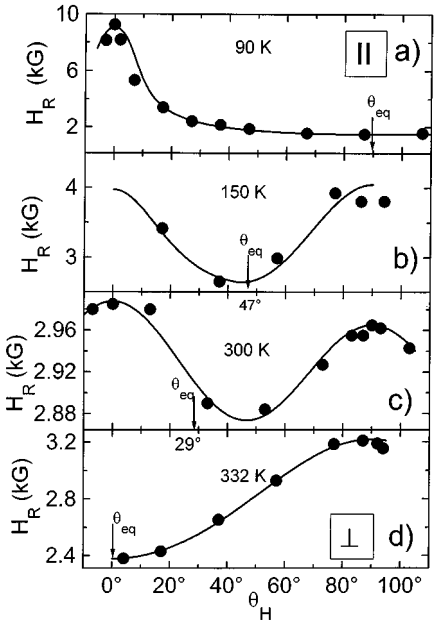


FIG. 1. Ferromagnetic resonance field as a function of the angle $\theta_H$ between the magnetic field and the film normal of 7.5 ML Ni/Cu(001) at four different temperatures recorded at 9 GHz. Note the different $y$-scales. $T_c = 430$ K.

185 K indicating a perpendicular easy axis. This transition is completely reversible and is observed for many heating and cooling cycles. Interestingly, the shape of these loops is quite different from the ones observed in Fe/Ag (001),[36] where a vanishing remanent magnetization $M_r$ is observed due to the formation of a stripe domain pattern. In our case we find $M_r \neq 0$, which indicates a different reversal mechanism. Although MOKE measurements are mostly used in the study of SRT, based on these hysteresis loops alone, it would be dif-

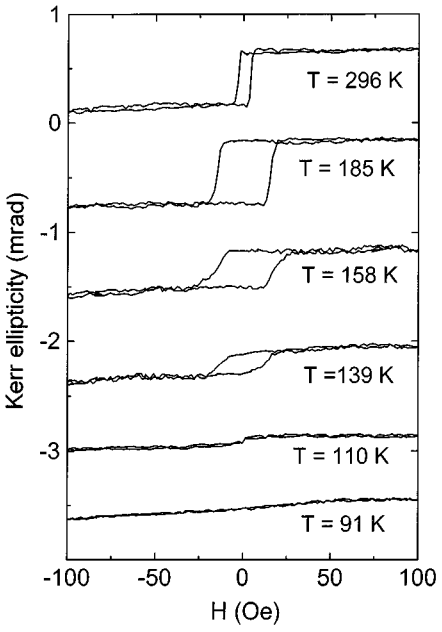


FIG. 2. Hysteresis loops measured for a 8.2 ML Ni/Cu(001) film with the magnetic field applied normal to the film plane. Temperatures as indicated. Loops are vertically offset for clarity.

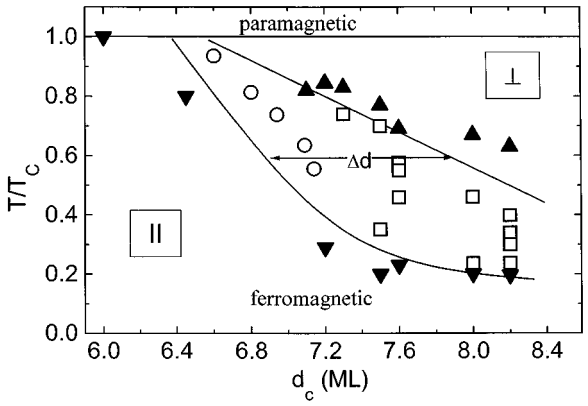


FIG. 3. Phase diagram for Ni/Cu(001): down triangles denote parallel, squares denote tilted, and up triangles denote perpendicular orientation of the magnetization. For open circles see text. Data at 8.2 ML are taken from Fig. 2. Solid lines are guide to the eyes, separating regions with parallel, tilted, and perpendicular spontaneous $M$.

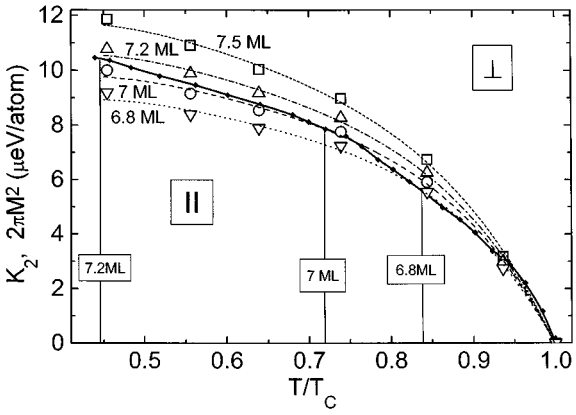


FIG. 4. Temperature dependence of shape anisotropy $2\pi M^2$ (solid line) of bulk Ni (Ref. 30) and second-order MAE $K_2=K_2^V+2K_2^S/d$ (open symbols). $K_2$ is calculated with experimental values (Ref. 21) for $K_2^V$ and $K_2^S$ at 6.8, 7.0, 7.2, and 7.5 ML. Note that a perpendicular magnetization is given for $K_2>2\pi M^2$. Reorientations can occur at the indicated temperatures.

ficult to distinguish a stable (single-domain) magnetization with a tilted equilibrium angle from a multidomain state. FMR measurements (Fig. 1) can answer this question unambiguously.

The result of our FMR and MOKE investigations is summarized in Fig. 3. Here, we show the orientation of the magnetization as a function of film thickness and reduced temperature $T/T_c(d)$, which is the thermodynamical relevant quantity. All data points except the ones of the 8.2 ML film (Fig. 2) are based on a large set of angular-dependent FMR measurements which were recorded at different thicknesses and $T/T_c(d)$. This involved also an accurate determination of $T_c$ for each layer. One can identify three stability regions of the spontaneous magnetization. The up (down) triangles represent measurements for which a perpendicular (parallel) orientation was found. The squares stand for equilibrium angles $0<\theta_{\mathrm{eq}}<90°$. For completeness, we have also included earlier results (open circles) which were analyzed in $K_2$ only.[37] The diagram shows that, for example at $d=7$ ML, a tilted orientation is found between $t=0.5$ and 0.85, while at $d=8$ ML the temperature interval is shifted to lower values. The solid lines, which are only guides to the eyes, mark the boundaries where the parallel ($M_\parallel$) or the perpendicular $M_\perp$ components of $M$ disappear. The broadest thickness-dependent SRT interval ($\Delta d\approx 1.5$ ML) is found at $T/T_c \approx 0.5$. The width of the SRT as a function of $T/T_c$ also changes. The maximum width is found around 7.6 ML. One should note that despite the decreased slope of the lower boundary ($d_c>7.6$ ML) the absolute temperature for the appearance of $M_\perp$ still decreases considerably, since $T_c(d)$ increases. For thicker films only $M$ with $\theta_{\mathrm{eq}}=0°$ was found in the experimentally checked temperature regime.

The results in Fig. 3 support the interpretation of a second-order phase transition with a continuous change of the angle of the magnetization.[19,20] Similar behavior has been discussed in the SRT of Co and Fe films, however, only in the reversed direction of thickness or temperature. Comparing the SRT in Co and Fe films and this SRT in Ni on Cu(001), we would like to point out that the choice of a unique order parameter for the three materials (like $M_\perp$ or the angle of the magnetization) poses a problem. For example, the order parameter $M_\perp$ for Ni/Cu becomes nonzero only *above* the critical temperature, which is unphysical. A full discussion on the nature of the order parameter, however, goes beyond the scope of the present work.

Figures 1 and 2 show experimentally an anomalous SRT. But what is the driving mechanism of the SRT in Ni/Cu(001)? Among the microscopic theories in the literature there is only one report[38] in which a transition from an in-plane phase to an out-of-plane phase with increasing temperature is calculated. However, the SRT is seen only in the absence of exchange interaction. Such a model is certainly not appropriate for a Ni ferromagnet. In a simple mean-field picture the magnetization is coupled to the anisotropy constants by some power-law dependence.[10,39] It has been calculated that the surface and volume magnetizations have different temperature dependences.[40] Consequently, the surface and volume anisotropies have a different temperature dependence too. With the experimentally determined $K_2^V(T)$ and $K_2^S(T/T_c)$ (Refs. 21 and 32) of Ni we calculate $K_2(T/T_c)$ (open symbols in Fig. 4) for different thicknesses and compare it with the shape anisotropy $2\pi M^2$ of bulk Ni (solid line).[30] In this simple (lowest order) estimate one has a parallel (perpendicular) easy axis for $K_2<2\pi M^2$ ($K_2>2\pi M^2$). As seen in Fig. 4 the different temperature dependences of $K_2^S$ and $K_2^V$ yield a $K_2(T/T_c)$ which can cross $2\pi M^2(T/T_c)$ in a narrow thickness interval, for example, at $d=6.8$ and 7 ML. $M$ changes from in-plane to perpendicular with increasing $T$. The reorientation temperature increases with decreasing film thickness, and below 6.8 ML an easy in-plane magnetization is expected for all temperatures. For 7.5 ML, on the other hand, one estimates a perpendicular orientation above $T/T_c>0.45$ and a parallel orientation only at very low temperatures. This model, which includes $K_2^S$ *and* $K_2^V$, describes very nicely the experimentally measured behavior (Fig. 3). Clearly, the complete phase diagram (Fig. 3) including tilted orientations cannot be explained by the second-order approach of Fig. 4.

In conclusion, we have determined experimentally the unusual phase diagram of the orientation of $M$ in fct Ni/Cu(001). With increasing temperature and increasing thickness a reorientation phase transition from an in-plane phase to a perpendicular phase is observed. Stable magnetization directions at intermediate out-of-plane angles are identified by FMR. The results are confirmed by polar Kerr effect measurements. The anomalous SRT is explained by the difference in the temperature dependence of the negative surface and the positive volume anisotropy energy in Ni/Cu(001), which was also measured. This shows that $K_2^V(T)$ should not be neglected in theoretical calculations of the SRT in thin films. Furthermore, as a function of $d$ and $T/T_c$ two boundaries are obtained for the appearance of the perpendicular component and for the disappearance of the parallel component of $M$.

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[1] R. Allenspach and A. Bischof, Phys. Rev. Lett. **69**, 3385 (1992).
[2] R. Allenspach, J. Magn. Magn. Mater. **129**, 160 (1994).
[3] A. Berger and H. Hopster, Phys. Rev. Lett. **76**, 519 (1996); J. Appl. Phys. **79**, 5619 (1996).
[4] U. Gradmann, Ann. Phys. (Leipzig) **17**, 91 (1966).
[5] G. Garreau, E. Beaurepaire, K. Ounadjela, and M. Farle, Phys. Rev. B **53**, 1083 (1996).
[6] Dongqi Li, M. Freitag, J. Pearson, Z. Q. Qiu, and S. D. Bader, Phys. Rev. Lett. **72**, 3112 (1994).
[7] D. P. Pappas, K.-P. Kämper, and H. Hopster, Phys. Rev. Lett. **64**, 3179 (1990).
[8] D. P. Pappas, C. R. Brundle, and H. Hopster, Phys. Rev. B **45**, 8169 (1992).
[9] P. J. Jensen and K. H. Bennemann, Phys. Rev. B **42**, 849 (1990).
[10] Y. Millev and J. Kirschner, Phys. Rev. B **54**, 4137 (1996).
[11] P. J. Jensen and K. H. Bennemann, Phys. Rev. B **52**, 16 012 (1995).
[12] P. J. Jensen and K. H. Bennemann, Solid State Commun. **100,** 585 (1996).
[13] A. Moschel and K. D. Usadel, Phys. Rev. B **49**, 12 868 (1994).
[14] D. K. Morr, P. J. Jensen, and K. H. Bennemann, Surf. Sci. **307-309**, 1109 (1994).
[15] D. Pescia and V. L. Pokrovsky, Phys. Rev. Lett. **65**, 2599 (1990).
[16] A. Hucht, A. Moschel, and K. D. Usadel, J. Magn. Magn. Mater. **148**, 32 (1995).
[17] X. Hu, R. Tao, and Y. Kawazoe, Phys. Rev. B **54**, 65 (1996).
[18] Ar. Abanov, V. Katatsky, V. L. Pokrovsky, and W. M. Saslow, Phys. Rev. B **51**, 1023 (1995).
[19] S. T. Chui, Phys. Rev. B **50**, 12 559 (1994).
[20] K. A. Müller, in *Structural Phase Transitions*, edited by K. A. Müller and H. Thomas, Vol. 45 (Springer, Berlin, 1991).
[21] K. Baberschke, Appl. Phys. A **62**, 417 (1996).
[22] B. Schulz and K. Baberschke, Phys. Rev. B **50**, 13 467 (1994).
[23] W. L. O'Brien and B. P. Tonner, Phys. Rev. B **49**, 15 370 (1994).
[24] F. Huang, M. T. Kief, G. J. Mankey, and R. F. Willis, Phys. Rev. B **49**, 3962 (1994).
[25] S. Z. Wu, G. J. Mankey, F. Huang, and R. F. Willis, J. Appl. Phys. **76**, 6434 (1994).
[26] G. Bochi, C. A. Ballentine, H. E. Inglefield, C. V. Thomson, R. C. O'Handley, Hans J. Hug, B. Stiefel, A. Moser, and H.-J. Güntherodt, Phys. Rev. B **52**, 7311 (1995).
[27] M. Farle, B. Mirwald-Schulz, A. N. Anisimov, W. Platow, and K. Baberschke, Phys. Rev. B **55**, 3708 (1997).
[28] A. Berghaus, M. Farle, Yi Li, and K. Baberschke, in *Magnetic Properties of Low-Dimensional Systems II*, edited by L. M. Falicov, F. Mejía-Lira, and J. L. Morán-López, Springer Proceedings in Physics Vol. 50 (Springer-Verlag, Berlin, 1990), p. 61.
[29] H. Fritzsche, J. Kohlhepp, H. J. Elmers, and U. Gradmann, Phys. Rev. B **49**, 15 665 (1994).
[30] M. B. Stearns, in *Magnetic Properties of Metals*, edited by H. P. J. Wijn, Landolt-Börnstein, Vol. III/19a (Springer, Berlin, 1986).
[31] G. André, A. Aspelmeier, B. Schulz, M. Farle, K. Baberschke, Surf. Sci. **326**, 275 (1995).
[32] M. Farle, W. Platow, A. N. Anisimov, B. Schulz, and K. Baberschke, J. Magn. Magn. Mater. **165**, 74 (1997).
[33] B. Schulz, A. Aspelmeier, and K. Baberschke, Vacuum **46**, 1189 (1995).
[34] S. Müller, B. Schulz, G. Kostka, M. Farle, K. Heinz, and K. Baberschke, Surf. Sci. **364**, 235 (1996); M. Ritter, M. Stindtmann, M. Farle, and K. Baberschke, *ibid.* **348**, 243 (1996).
[35] J. Shen, J. Giergiel, and J. Kirschner, Phys. Rev. B **52**, 8454 (1995).
[36] A. Berger and R. P. Erickson, J. Magn. Magn. Mater. **165,** 70 (1997).
[37] B. Schulz, Ph.D. thesis, Freie Universität, Berlin, 1995.
[38] A. B. MacIsaac, J. P. Whitehead, K. De'Bell, and P. H. Poole, Phys. Rev. Lett. **77**, 739 (1996).
[39] H. B. Callen and E. Callen, J. Phys. Chem. Solids **27**, 1271 (1966).
[40] P. J. Jensen, H. Dreyssé, and K. H. Bennemann, Surf. Sci. **269/270**, 627 (1992).