PHYSICAL REVIEW B VOLUME 50, NUMBER 18 1 NOVEMBER 1994-II

Crossover from in-plane to perpendicular magnetization in ultrathin Ni/Cu(001) films

B. Schulz and K. Baberschke
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

(Received 12 July 1994)

The easy axis of magnetization in Ni/Cu(001) films exhibits a crossover from in-plane to perpendicular orientation with *increasing* film thickness. This reorientation at ≈7 monolayers, observed by ferromagnetic resonance, is substantially different from previous findings for Fe and Co films and can be extrapolated from thin-film data. The artificial lattice structure of Ni on Cu yields within magnetoelasticity theory a volume anisotropy of 29 μeV/atom agreeing perfectly with experiment. In thinner films the surface anisotropy of −77 μeV/atom dominates.

The study of ferromagnetic films in the monolayer (ML) regime offers the possibility to explore magnetism in two-dimensional systems, where a long-range order is stabilized by anisotropy energies, so that the film is no longer Heisenberglike. Thus deeper understanding of low-dimensional systems requires further insight on anisotropy energies. However, to calculate them, knowledge of the real crystallographic structure and the corresponding band structure would be needed. The present system turns out to be an ideal case.

In general, for ultrathin films an in-plane easy axis of M is expected owing to the demagnetizing energy. In the literature there are exceptions: A change from a perpendicular orientation of the easy axis of M for film thickness d below a few ML to an in-plane orientation for larger d has been reported for Fe/Ag(001),[1] Fe/Cu(001),[2,3] and Co/Au(111).[4,5] The interpretation is straightforward: The surface anisotropy can overcome the shape anisotropy $4\pi M$ for few ML's ($\approx 1-5$ ML), yielding a magnetization perpendicular to the film if the contribution of the surface is positive. With increasing thickness the effective surface contribution decreases, leading to a switching of M to in-plane orientation. In this paper we present the *reverse case,* namely, a reorientation of M from in plane to out of plane with *increasing* thickness of a Ni/Cu(001) film. This finding is of general interest for two reasons: (i) For magnetic engineering, films of $\approx 7-60$ ML are much more favorable for perpendicular recording devices than those of just one ML. (ii) From a fundamental point of view, a model system with an artificial structure imposed by the substrate is realized up to a critical thickness being very large in the present system. For this prototype of a well-defined lattice free of dislocations, a full quantitative explanation of the measured anisotropies is achieved by taking into account magnetoelasticity effects with Ni bulk parameters.

Ferromagnetic resonance (FMR) measurements were carried out to determine the anisotropy energies and thus the easy axis of M from an analysis of the temperature and angular dependence of the resonance field H_R. The free-energy density E in an applied dc magnetic field H for a film with tetragonal symmetry is given by (Fig. 1)

$$\begin{aligned}E=&-HM[\sin\theta\sin\theta_H\cos(\varphi-\pi/4)+\cos\theta\cos\theta_H]\\&+2\pi M^2\cos^2\theta-K_u\cos^2\theta-\tfrac{1}{2}K_{1\perp}\cos^4\theta\\&-\tfrac{1}{2}K_{1\parallel}\tfrac{1}{4}(3+\cos^4\varphi)\sin^4\theta\ .\end{aligned}\tag{1}$$

The first term describes the Zeeman energy, the second one the demagnetizing energy. K_u and $K_{1\perp}$ represent the perpendicular uniaxial anisotropy of second and fourth order, respectively, and the fourfold in-plane anisotropy is given by $K_{1\parallel}$.[6] Keeping the azimuth angle fixed at $\varphi_H=\pi/4$, the general FMR resonance condition[7] yields for $\theta_H=\pi/2$ and $\theta_H=0$, respectively:

$$\left[\frac{\omega}{\gamma}\right]^2=\left[H_{R\parallel}-\frac{2K_{1\parallel}}{M}\right]\times\left[H_{R\parallel}+\frac{K_{1\parallel}}{M}+H_{\rm an}\right],\tag{2a}$$

$$\frac{\omega}{\gamma}=H_{R\perp}-H_{\rm an}+\frac{2K_{1\perp}}{M},\tag{2b}$$

where $H_{\rm an}$ is the anisotropy field:

$$H_{\rm an}=4\pi M-\frac{2K_u}{M}\ .\tag{3}$$

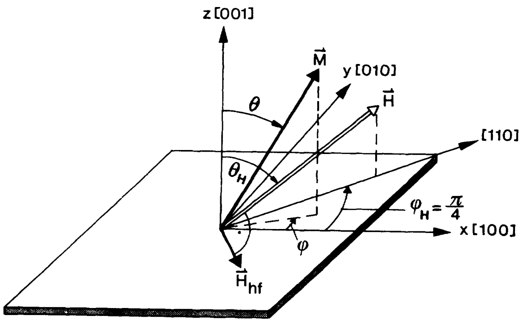

FIG. 1. Coordinate system used in this paper. The microwave field $H_{\rm hf}$ lies always in the film plane, which equals the x,y plane. The dc magnetic field H can be varied continuously in the [110], z plane resulting in a specific orientation of the magnetization M given by (θ,φ). Here the case of a perpendicular easy axis of M is shown, therefore, $\theta<\theta_H$.

Commonly the effective anisotropy constants are separated in thickness-dependent and thickness-independent terms:

$$K^{\text{eff}}=K^{V}+\frac{2K^{S}}{d}\ . \tag{4}$$

In the pioneering work,[8] K^V describes the magnetocrystalline bulk anisotropy and K^S the Néel-type[9] surface term. In recent work it turned out that magnetostrictive contributions have to be considered in addition, caused by the formation and subsequent release of lateral strains: For Ni/Cu(001) an extended regime of pseudomorphic growth occurs below a critical thickness d_c, where the strain is given by the mismatch η between film and substrate and is thus thickness independent. Therefore, K^V is not identical to the anisotropy energy in the unperturbed bulk material. The magnetocrystalline anisotropy for Ni single crystals ($K^{\text{bulk}}\approx-0.39$ μeV/atom at 300 K), for example, is two orders of magnitude smaller than K^V calculated below. Above d_c the strain will be reduced by misfit dislocations, resulting in a variation of the magnetostrictive anisotropy as approximately $1/d$, thus in an effective "surface" contribution K^S,[10,11] which is not located at the surface.

The magnetostrictive anisotropy is estimated within magnetoelasticity theory. In the pseudomorphic regime it is directly correlated with the lateral (tensile) stress ε_1 exerted by the substrate and the associated tetragonal distortion ε_2 (compressive stress). Minimizing the elastic energy with respect to ε_2 for a given ε_1 yields

$$\varepsilon_2=-\frac{2c_{12}}{c_{11}}\varepsilon_1\ , \tag{5}$$

where c_{11} and c_{12} are the cubic elastic stiffness constants. ε_1 is given by the mismatch η between Ni and Cu: $\varepsilon_1=-\eta=2.5\%$. With c_{11} and c_{12} from Ref. 12 $\varepsilon_2=-3.2\%$ is calculated (at 300 K). The existence of this tetragonal distortion is experimentally confirmed in the ML regime[13] and also for $d>28$ ML.[14] From the magnetoelastic energy for a cubic lattice, the perpendicular uniaxial anisotropy is estimated:

$$K_u^V=3/2\lambda_{100}(c_{11}-c_{12})(\varepsilon_2-\varepsilon_1)\ , \tag{6}$$

where λ_{100} is the magnetostriction constant. Using the values for bulk Ni at 300 K,[12] $K_u^V=29(5)$ μeV/atom results.

Ni was deposited at 300 K to avoid interdiffusion. The base pressure of 4×10^{-11} mbar increased during evaporation to 3×10^{-10} mbar. The film thickness d was determined by means of a quartz microbalance and Auger electron spectroscopy. Analysis of the Auger amplitudes[15] reveals that Ni evaporated on Cu(001) at 300 K grows layer by layer, in agreement with the literature.[13,16,17] The observation of sharp low-energy electron-diffraction (LEED) patterns with a low background in combination with a very narrow FMR linewidth for ultrathin films [190 G at 9 GHz (Ref. 15) in comparison to 130 G for bulk Ni (Ref. 18) and to 350 G for 7 ML Ni/W (Ref. 19)], proves the good quality of the epitaxial growth. From the linewidth the existence of very large magnetically homogeneous domains can be deduced having a lateral dimension of at least 200 to 600 nm.[15]

FMR was measured *in situ* at 9 GHz with the external field H lying in the [110], z plane. From the FMR signal, the resonance field H_R as well as the FMR linewidth can be extracted. In this paper we focus on H_R (Fig. 2), which yields directly H_{an} in absolute magnetic field units via Eqs. (2a) and (2b). Neglecting at first anisotropies of fourth order, H_{an}, which contains two competing contributions [Eq. (3)] determines the orientation of M. An in-plane easy-axis magnetization is favored if $H_{\text{an}}>0$, whereas $H_{\text{an}}<0$ gives rise to a spontaneous out-of-plane orientation of M. The latter case occurs if K_u is positive and sufficiently large, as observed for an 8-ML film (Fig. 2). H_{an} and the corresponding anisotropy constants were calculated by taking values of bulk Ni for $M(T/T_c)$.[20] Values of H_{an} for different film thicknesses need to be compared at the same reduced temperature $t=T/T_c$ because of the strong thickness dependence of $T_c(d)$.[15,19] The anisotropy fields H_{an} for $d=3-6.3$ ML, measured with the field oriented parallel to the film at $t=0.9$, are all positive. This corresponds to an in-plane orientation of M. Using Eq. (3), $2K_u/M$ is calculated and plotted in Fig. 3 as function of $1/d$ yielding a linear behavior. The full circles (●) are measured at $t=0.9$. For $1/d\approx0.15$ ML^{-1} the field $2K/M$ equals $4\pi M=3.9$ kG. Therefore, we *extrapolate* that for larger thicknesses M is switched to an out-of-plane orientation. Indeed the data (■) prove this. This anomalous thickness dependence, namely, a crossover from in-plane to out-of-plane orientation of M at 7 ML, is opposite to previous findings.[1-3] It is a novel experiment with regard to the fact that from thin-film data (●), the thickness at which M would flip can be estimated, namely, at ≈7 ML.

From the linear behavior (Fig. 3) we conclude that Ni/Cu(001) grows in a pseudomorphic way up to 8–9 ML, in agreement with the observed LEED patterns and with Refs. 21 and 22. This finding clarifies previous investigations on the pseudomorphic growth of

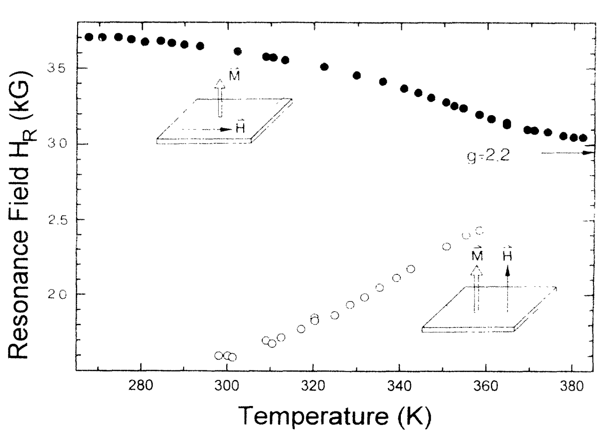

FIG. 2. $H_R(T)$ for an 8 ML film ($T_c\approx460$ K) of Ni/Cu(001) with perpendicular easy axis of M. The direction of the external magnetic field was either parallel (●) or perpendicular (○) to the film plane.

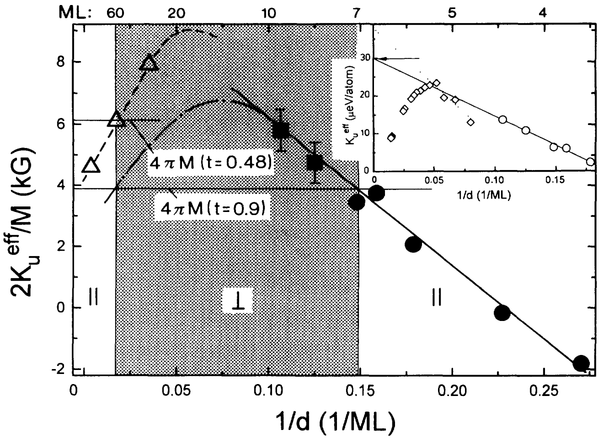

FIG. 3. Perpendicular uniaxial anisotropy field vs $1/d$ at $t=0.9$ (●). The squares (■) are extrapolated to $t=0.9$ from original data measured at $t \approx 0.6-0.83$. The intersection of the straight line with the demagnetizing energy at $t=0.9$ defines the reorientation transition at ≈ 7 ML. The data at larger thickness (Δ) are taken from Ref. 27 at $t=0.48$ showing the second crossover to in-plane magnetization again. The dashed and dash-dotted lines are guides for the eye. Inset: Thickness dependence of the anisotropy constant K_u^{eff} at 300 K yielding (open circles) $K_u^V=30(3)$ μeV/atom and $K_u^S=-77$ μeV/atom according to Eq. (4). The diamonds correspond to measurements on Cu/Ni/Cu sandwiches from Ref. 22.

Ni/Cu(001).[23] Only in this regime does the slope really reveal the surface anisotropy and the intersection with the ordinate axis yielding the magnetostrictive anisotropy induced by strain owing to mismatch. In the inset of Fig. 3, K_u at 300 K is plotted, so that the results linearly extrapolated (solid line) from the pseudomorphic regime are comparable to the calculation of the magnetoelastic anisotropy [Eq. (6)]. From the inset we get $K_u^V=30(3)$ μeV/atom and $K_u^S=-77$ μeV/atom. This agrees perfectly well with the calculated K_u^V of 29(5) μeV/atom. Thus the large positive volume anisotropy may be explained within the magnetoelasticity model assuming a tetragonal distortion due to pseudomorphic growth. Comparing this result to a very recent investigation of Cu/Ni/Cu(001) sandwiches[22] (diamonds in the inset of Fig. 3), a larger value for $K_u^V=38$ μeV/atom has been extrapolated (dotted line). This difference to theory is attributed in Ref. 22 to the unknown magnetoelastic constants in thin films. Another interpretation of their data is to ignore one single data point taken at 13 ML. Then the data fit well with our straight line, which reflects indeed the pseudomorphic region, since the emphasis of our experiment lies on the very-thin film limit. (In Ref. 22 the pseudomorphic region is extended up to ≈ 24 ML due to the influence of the Cu coverlayer.) Recent calculations of K_u^S (Ref. 24) yield a value of -860 μeV/atom by taking into account the effects of the filling of the 3d band and a crystal-field energy $\Delta=0.5$ eV from Ni(111) band-structure calculations. However, Δ is not well known for thin films, and $\Delta \approx -0.13$ eV would agree better with the experimental K^S. Furthermore, in contrast to theoretical calculations the measurements are performed at 300 K and yield the averaged anisotropy of both the Ni/Cu interface and the Ni surface. Further investigations are needed to separate surface anisotropies at metal/metal interfaces from metal/vacuum surfaces.[25] Another mechanism, which can modify K^S, is the surface roughness, which is negligible for our films.[15]

The particular signs of K^V and K^S, namely, a positive value of K^V, favoring an out-of-plane magnetization, in combination with a negative value of K^S, explain the unusual thickness-dependent behavior of the spontaneous magnetization orientation: For very thin films the demagnetizing energy as well as the anisotropy term $2K_u/M$ force M into the film plane because of a dominating negative surface contribution. Above 7 ML, the influence of K^S has decreased so that the large positive strain-induced volume anisotropy can manage a perpendicular orientation of M. This emphasizes the role of stress in ultrathin films. The results of an investigation by Gradmann,[26] 30 years ago, on Ni(111) films covered with Cu and prepared in 10^{-7} Torr vacuum are in accord with the present work and may be interpreted in a similar manner. If we consider Fe/Cu or Fe/Ag, in contrast to Ni, a large positive surface contribution K_u^S is responsible for the perpendicular orientation, combined with a negative magnetostrictive contribution to K_u^V due to a reverse sign of λ_{100}. This explains the reverse thickness behavior.

Now we turn to thicknesses larger than d_c, where the pseudomorphic growth is supposed to cease. Fortunately this was investigated recently.[14,22,27] A perpendicular magnetization for 28 ML and an in-plane magnetization for 56 ML of Cu/Ni/Cu(001) sandwiches[27] (Δ in Fig. 3) were measured. Above d_c the $K(1/d)$ curve should deviate from the linear behavior towards lower K values, taken at the same reduced temperature (dash-dotted line in Fig. 3) due to strain relaxation. The data from Ref. 27 (dashed line) fit well with this model. Since they were measured at lower t, they are shifted to higher values. This model is totally confirmed by recent magneto-optic Kerr effect (MOKE) measurements on Cu/Ni/Cu sandwiches[22] (diamonds in the inset of Fig. 3), showing a second linear regime with reversed slope due to the positive magnetoelastic contribution. This is here only an effective surface anisotropy, since it can be assumed that $\varepsilon=-\eta d_c/d$ (Refs. 10 and 21) and that the magnetostrictive volume contribution is negligible above a certain thickness. The misfit-induced strains are thus relieved only very slowly,[14] resulting in an out-of-plane orientation up to ≈ 56 ML. A perpendicular orientation of M between 7 and 56 ML is an interesting result. The crossovers are not sharp but depend on temperature. It is worth noticing that a separation in K^V and K^S with a well-defined assignment of the magnetostrictive contributions to K^V only and thus an interpretation of K^S as being a Néel-type anisotropy is not possible in the thickness range 28–280 ML, since it is far away from the pseudomorphic regime. This is illustrated by the reverse thickness dependence of the anisotropy fields.[27] In this region a correlation of the anisotropies with stress requires measurements of the thickness-dependent lattice distortions.

To confirm this unusual behavior we turn back to Fig. 2. The pronounced variation of H_R with temperature below T_c reflects the temperature dependence of both M and the anisotropy energies. Generally, if the field is oriented parallel (perpendicular) to M, H_R is smaller (larger) than $\omega/\gamma=2.95$ kG (corresponding to $g=2.2$) and approaches this value with increasing temperature (as $T\rightarrow T_c$). Thus Fig. 2 unambiguously shows that the easy axis of M has an out-of-plane orientation. In order to decide whether M is really oriented perpendicularly or tilted with respect to the film plane, FMR is a very useful method: The full angular dependence of H_R can be measured (Fig. 4). The smallest resonance field is achieved at $\theta_H=0°$. This reveals without doubt that the spontaneous magnetization is oriented *perpendicularly* to the film above 7 ML. Moreover, the validity of the uniaxial anisotropy model and the importance of fourth-order anisotropy constants can be seen from Fig. 4. The experimental data have been fitted to the angular dependence of H_R. The only fit parameters are K_u, $K_{1\perp}$, and $K_{1\parallel}$. A second-order contribution K_u is not sufficient to describe the full angular dependence of H_R (dotted line), thus it is necessary to introduce fourth-order contributions. Optimizing the fit to the data yields $K_u=10.5$ μeV/atom, $K_{1\perp}=0.14$ μeV/atom, and $K_{1\parallel}=-1.91$ μeV/atom (solid line). $K_{1\perp}$ and $K_{1\parallel}$ have the same order of magnitude as the fourth-order magnetocrystalline bulk anisotropy. In these thin films, the easy axis in the film plane is the [110] axis, as indicated by the negative sign of $K_{1\parallel}$.

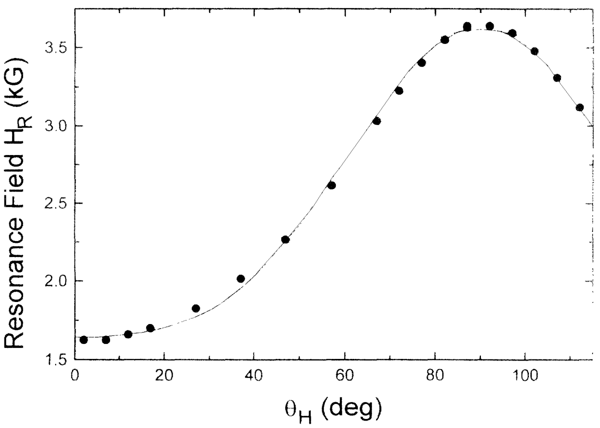

FIG. 4. Resonance field at 300 K vs θ_H for an 8-ML film. The dotted and solid lines are calculated by taking into account the equilibrium condition for M together with the general resonance condition which can be derived from Eq. (1). Taking $M=449$ G and $g=2.18$ (Ref. 28), the fits are calculated with $K_u=10.5$ μeV/atom, $K_{1\perp}=K_{1\parallel}=0$ for the dotted line and $K_u=10.5$ μeV/atom, $K_{1\perp}=0.14$ μeV/atom, $K_{1\parallel}=-1.91$ μeV/atom for the solid line.

In conclusion, we have shown that a perpendicular easy axis of the magnetization *above* 7 ML in Ni/Cu(001) can be extrapolated from the anisotropy constants measured at small thicknesses and is experimentally confirmed. With respect to other systems with perpendicular magnetization, this finding represents an anomalous thickness behavior and can be quantitatively explained by the present FMR investigation (large K_u^V and negative sign of K_u^S). The intrinsic uniaxial anisotropy caused by the tetragonal Ni lattice is the reason for perpendicular easy axis, in contrast to other systems where K^S is the driving force. Below 7 ML the stronger influence of the surface anisotropy K_u^S leads to an in-plane magnetization. In the pseudomorphic growth regime K_u^S and K_u^V can be directly correlated to the Néel surface anisotropy and the mismatch-induced magnetostrictive anisotropy, respectively. In this region, knowledge of the artificial lattice structure allows one to estimate the latter by magnetoelasticity theory in perfect agreement for the first time with the experimentally determined K_u^V. Concerning K_u^S, further *ab initio* calculations are needed. The present study also demonstrates that from magnetic measurements structural information may be deduced.

The authors would like to thank R. Schwarzwald and M. Farle for helpful discussions and A. Aspelmeier for carefully reading the manuscript. We thank U. Gradmann for bringing Ref. 26 to our attention. This work was supported in part by the DFG Sfb 290, TP A2.

---

[1] Z. Q. Qiu, J. Pearson, and S. D. Bader, Phys. Rev. Lett. **70**, 1006 (1993).

[2] R. Allenspach and A. Bischof, Phys. Rev. Lett. **69**, 3385 (1992).

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

[4] R. Allenspach, M. Stampanoni, and A. Bischof, Phys. Rev. Lett. **65**, 3344 (1990).

[5] C. Chappert, K. Le Dang, P. Beauvillain, H. Hurdequint, and D. Renard, Phys. Rev. B **34**, 3192 (1986).

[6] B. Heinrich, J. F. Cochran, A. S. Arrott, S. T. Purcell, K. B. Urquhart, J. R. Dutcher, and W. F. Egelhoff, Jr., Appl. Phys. A **49**, 473 (1989).

[7] J. Smit and H. C. Beljers, Philips Res. Rep. **10**, 113 (1955).

[8] U. Gradmann, J. Magn. Magn. Mater. **54-57**, 733 (1986).

[9] L. Néel, J. Phys. Rad. **15**, 225 (1954); **15**, 376 (1954).

[10] P. Bruno, and J.-P. Renard, Appl. Phys. A **49**, 499 (1989), and references therein.

[11] B. M. Clemens, R. Osgood, A. P. Payne, B. M. Lairson, S. Brennan, R. L. White, and W. D. Nix, J. Magn. Magn. Mater. **121**, 37 (1993).

[12] S. Chikazumi and S. H. Charap, *Physics of Magnetism* (Wiley, New York, 1964).

[13] Y. Idzerda, and G. A. Prinz, Surf. Sci. **284**, L394 (1993).

[14] Chin-An Chang, J. Appl. Phys. **68**, 4873 (1990).

[15] B. Schulz, R. Schwarzwald, and K. Baberschke, Surf. Sci. **307-309**, 1102 (1994). In this work it is shown that a distribution of demagnetizing factors and thus a lower limit for a finite domain size can be obtained by taking into account the FMR linewidth.

[16] C. Stuhlmann and H. Ibach, Surf. Sci. **219**, 117 (1989).

[17] L. H. Tjeng, Y. U. Idzerda, P. Rudolf, F. Setter, and C. T. Chen, J. Magn. Magn. Mater. **109**, 288 (1992).

[18] S. M. Bhagat and P. Lubitz, Phys. Rev. B **10**, 179 (1974). See also the FMR of Cu-Ni alloys: L. H. Bennett, D. S. Lashmore, M. P. Daniel, M. J. Kaufman, M. Rubinstein, P. Lubitz, O. Zadok, and J. Yahalom, J. Magn. Magn. Mater. **67**,

239 (1987).

[19] Yi Li and K. Baberschke, Phys. Rev. Lett. **68**, 1208 (1992); Yi Li, M. Farle, and K. Baberschke, Phys. Rev. B **41**, 9596 (1990).

[20] *Magnetic Properties of Metals,* Vol. 19a of Landolt-Börnstein (Springer, Berlin, 1986).

[21] J. W. Matthews and J. L. Crawford, Thin Solid Films **5**, 187 (1970).

[22] R. Jungblut, M. T. Johnson, J. aan de Stegge, A. Reinders, and F. J. A. den Broeder, J. Appl. Phys. **75**, 6424 (1994).

[23] D. W. Gidley, Phys. Rev. Lett. **62**, 811 (1989).

[24] P. Bruno, Phys. Rev. B **39**, 865 (1989).

[25] For more details, see B. Schulz, A. Aspelmeier, and K. Baberschke, Vacuum (to be published).

[26] U. Gradmann, Ann. Phys. **17**, 91 (1966).

[27] R. Naik, C. Kota, J. S. Payson, and G. L. Dunifer, Phys. Rev. B **48**, 1008 (1993).

[28] E. P. Wohlfarth, *Ferromagnetic Materials* (North-Holland, Amsterdam, 1980), Vol. 1.

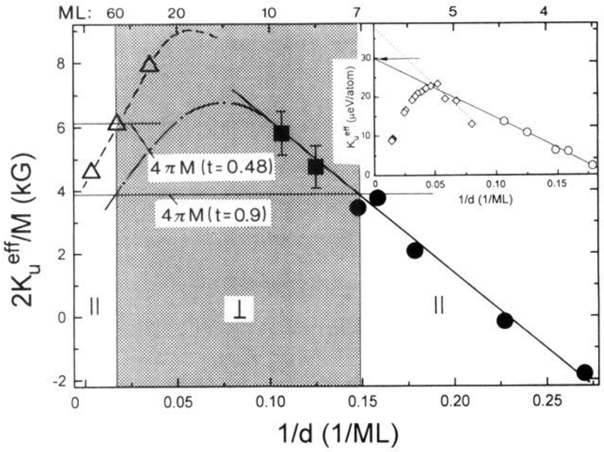

FIG. 3. Perpendicular uniaxial anisotropy field vs $1/d$ at $t=0.9$ (●). The squares (■) are extrapolated to $t=0.9$ from original data measured at $t \approx 0.6-0.83$. The intersection of the straight line with the demagnetizing energy at $t=0.9$ defines the reorientation transition at ≈ 7 ML. The data at larger thickness (Δ) are taken from Ref. 27 at $t=0.48$ showing the second crossover to in-plane magnetization again. The dashed and dash-dotted lines are guides for the eye. Inset: Thickness dependence of the anisotropy constant K_u^{eff} at 300 K yielding (open circles) $K_u^V=30(3)$ μeV/atom and $K_u^S=-77$ μeV/atom according to Eq. (4). The diamonds correspond to measurements on Cu/Ni/Cu sandwiches from Ref. 22.