Angular dependence of perpendicular magnetic surface anisotropy and the spin-reorientation transition

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For a complete description of out-of-plane magnetic surface anisotropy and its angular dependence, higher-order terms are needed beyond the quadratic Néel-type approximation. The spin-reorientation transition between perpendicular and in-plane magnetization is influenced by these higher-order terms in an elementary manner. Second- and fourth-order terms of the magnetic surface anisotropy were determined by torsion-oscillation magnetometry for uncovered Fe(110) films prepared on Cr(110), and for Pd-covered Co films prepared on Pd(111). These samples show different types of the spin-reorientation transition.

A cornerstone in the physics of ultrathin magnetic films is the theorem of Mermin and Wagner[1] on the absence of long-range order in two-dimensional (2D) isotropic Heisenberg systems. In 2D systems, long-range order must be triggered by anisotropies, contrary to 3D systems, where it exists without anisotropy. This might seem academic because ultrathin films are just systems with strong intrinsic anisotropies, the leading terms being given by shape anisotropy, which strongly supports in-plane magnetization, and magnetic surface anisotropy (MSA), which was predicted by Néel[2] as a result of the break of local symmetry in the interfaces and may support in-plane or perpendicular magnetization. As a rule, long-range order is stabilized in ultrathin films by those strong anisotropies. An interesting situation results when MSA supports perpendicular magnetization and with decreasing thickness may even overcompensate shape anisotropy, resulting in perpendicular magnetization. At a critical thickness, shape and surface anisotropy cancel in some sense; it is a subject of intense present discussion whether the resulting "spin-reorientation transition" between in-plane and perpendicular magnetization is connected with a loss or weakening of long-range order. The problem is very much complicated by the long-range character of magnetostatic interactions. Nevertheless, fundamental theoretical papers[3-5] predict a drop of the Curie temperature near the transition. Perpendicular magnetization as a result of perpendicular MSA has been detected first in NiFe(111) on Cu(111) (Ref. 6) and is now known from many systems such as hcp Co(0001) on Au(111),[7-9] fcc Co(111) on Pd(111),[10-12] Pt(111),[10] and Cu(111),[13] Fe(110) on Au(111),[14] and Fe on Cu(100),[15,16] and Ag(100).[17-19] Near the spin-reorientation transition, a loss of remanent magnetization[15,19] and the evolution of specific fine-grained domains[9,16] was observed; the drop of T_c remains to be detected.

In this paper we address two basic problems of perpendicular magnetization and of the spin-reorientation transition which apparently have been neglected so far. The first problem is the angular dependence of MSA. Néel used the simplest possible ansatz, $\sigma(\vartheta)=K_S\cdot\cos^2\vartheta$, with a polar angle ϑ between magnetization and surface normal, and a surface anisotropy constant K_S. This approximation is used throughout the literature. In cases where higher-order terms in film anisotropies have been observed, e.g., Refs. 20, 9, and 21, it has been tacitly assumed that MSA is given by the bare Néel term. To our knowledge, higher-order terms of MSA were taken into consideration only by Purcell *et al.*;[11] however, they could not determine them experimentally. We will show how higher-order terms of MSA can be determined by torsion-oscillation magnetometry,[22] (TOM) and that they exist in uncovered Fe(110) films on Cr(110), for which we detected perpendicular magnetization recently,[23] and in Pd-covered Co films on Pd(111), for which perpendicular magnetization has been known for a long time.[10-12] The second problem then is whether and how the nature of the spin-reorientation transition is influenced by the angular structure of $\sigma(\vartheta)$. We will show that it depends on higher-order terms in an elementary manner, resulting in different types of the transition. Apparently, the one with a literal disappearance of anisotropy, which is assumed in theoretical models, is a rare exception. Our experimental samples represent different types of the transition.

As a basis for the discussion of magnetic anisotropies in a film of thickness t, we consider the anisotropic part of the magnetic free energy $F(\vartheta,\varphi)$ per film area A, in a magnetically saturated state, depending on the polar angle ϑ and the azimuth φ of the magnetization. In this paper, we focus on out-of-plane anisotropies, that means on the dependence on ϑ only, and therefore neglect the dependence on φ. Hence we discuss the results of measurement in a fixed azimuth φ_0, given by the external field. For brevity, we use $F(\vartheta,\varphi_0)=F(\vartheta)$, and $\sigma(\vartheta)=\sigma^{(1)}(\vartheta)+\sigma^{(2)}(\vartheta)$ as an abbreviation for the total surface anisotropy of the film, composed of contributions from both interfaces. A general ansatz for the free energy per area is then given by

$$F(\vartheta)/A=[(J_s^2/2\mu_0)\cdot\cos^2\vartheta+f(\vartheta)]\cdot t+\sigma(\vartheta)\ , \quad (1)$$

where $J_s^2/2\mu_0$ is the shape anisotropy, $f(\vartheta) = f_K(\vartheta) + f_\varepsilon(\vartheta)$ is a nonmagnetostatic volume anisotropy, composed of a magnetocrystalline term $f_K(\vartheta)$ and a strain term $f_\varepsilon(\vartheta)$, and $\sigma(\vartheta)$ is the surface anisotropy. All quantities are taken for a special fixed azimuth φ_0.

The usual discussion of MSA is based on Néel's quadratic ansatz $\sigma(\vartheta) = K_S \cdot \cos^2\vartheta$. Shape anisotropy as the dominating volume term is proportional to $\cos^2\vartheta$ too, and the same can be assumed for strain contributions $f_\varepsilon(\vartheta)$. It is then convenient to neglect higher-order terms in $f_K(\vartheta)$, resulting in $f(\vartheta) = K_V \cdot \cos^2\vartheta$ with a volume anisotropy constant K_V. One then obtains, as a quadratic approximation of Eq. (1),

$$F(\vartheta)/A = \{[J_s^2/2\mu_0 + K_V]\cdot t + K_S\} \cdot \cos^2\vartheta \ . \tag{2}$$

Because the volume term is dominated by shape anisotropy, it is always positive, that means it favors in-plane magnetization. The precondition of perpendicular anisotropy is therefore a negative value of K_S, which then favors perpendicular magnetization; we assume $K_S < 0$ in the following. The magnetization then switches from in-plane to perpendicular orientation at a critical thickness $t_c = (-K_S)/[J_s^2/2\mu_0 + K_V]$. The disappearance of anisotropy at t_c results in the weakening or loss of long-range order mentioned above. For an experimental determination of film anisotropies one measures, in a couple of experimental methods, the second derivatives $F_{\vartheta\vartheta}(\pi/2)$ and $F_{\vartheta\vartheta}(0)$ near the energetic extrema at $\vartheta = \pi/2$ and $\vartheta = 0$, respectively. These quantities are taken from the initial slope of hard axis loops, or in TOM from the period of oscillation; tightly related quantities are measured in ferromagnetic resonance or Brillouin scattering. From the quadratic approximation of Eq. (2), one easily obtains

$$F_{\vartheta\vartheta}(\pi/2)/A = -F_{\vartheta\vartheta}(0)/A = \{[J_s^2/\mu_0 + 2K_V]\cdot t + 2K_S\} \ .$$

By TOM or hard axis loops, both second derivatives can be measured only if they are positive. One then obtains $F_{\vartheta\vartheta}(\pi/2)/A$ for $t > t_c$ and $-F_{\vartheta\vartheta}(0)/A$ for $t < t_c$ and presents them in one common plot versus t, resulting in $2K_S$ from the axial section and $[J_s^2/\mu_0 + 2K_V]$ from the slope.

How must this scheme be modified when the quadratic approximation is lost? The second derivatives $F_{\vartheta\vartheta}(\pi/2)/A$ and $F_{\vartheta\vartheta}(0)/A$ remain the primary quantities of measurement, but they are now connected with parameters of volume and surface anisotropies which must be derived from the general expression of Eq. (1) as

$$F_{\vartheta\vartheta}(\pi/2)/A = [(J_s^2/\mu_0) + f_{\vartheta\vartheta}(\pi/2)]\cdot t + \sigma_{\vartheta\vartheta}(\pi/2) \tag{3a}$$

and

$$F_{\vartheta\vartheta}(0)/A = [-(J_s^2/\mu_0) + f_{\vartheta\vartheta}(0)]\cdot t + \sigma_{\vartheta\vartheta}(0) \ . \tag{3b}$$

Using fourth-order approximations

$$\sigma(\vartheta) = K_{S,2}\cos^2\vartheta + K_{S,4}\sin^2\vartheta\cdot\cos^2\vartheta$$

and

$$f(\vartheta) = K_{V,2}\cos^2\vartheta + K_{V,4}\sin^2\vartheta\cdot\cos^2\vartheta \ ,$$

these equations can be rewritten as

$$F_{\vartheta\vartheta}(\pi/2)/A = [(J_s^2/\mu_0) + 2(K_{V,2} + K_{V,4})]\cdot t + 2(K_{S,2} + K_{S,4}) \tag{4a}$$

and

$$-F_{\vartheta\vartheta}(0)/A = [(J_s^2/\mu_0) + 2(K_{V,2} - K_{V,4})]\cdot t + 2(K_{S,2} - K_{S,4}) \ . \tag{4b}$$

For the evaluation of the experimental data, it is again convenient to commonly plot $F_{\vartheta\vartheta}(\pi/2)/A$ and $-F_{\vartheta\vartheta}(0)/A$ versus t, to obtain surface anisotropies from the axial sections and volume anisotropies from the slope, as shown in Fig. 1.

The spin-reorientation transition is now characterized by two critical thicknesses,

$$t_{c,1} = \sigma_{\vartheta\vartheta}(0)/[J_s^2/\mu_0 - f_{\vartheta\vartheta}(0)] = -(K_{S,2} - K_{S,4})/[J_s^2/2\mu_0 + K_{V,2} - K_{V,4}] \tag{5a}$$

and

$$t_{c,2} = -\sigma_{\vartheta\vartheta}(\pi/2)/[J_s^2/\mu_0 + f_{\vartheta\vartheta}(\pi/2)] = -(K_{S,2} + K_{S,4})/[J_s^2/2\mu_0 + K_{V,2} + K_{V,4}] \ . \tag{5b}$$

They coincide in the quadratic approximation only. In the general case, their difference depends more sensitively on $\sigma_{\vartheta\vartheta}$ than on $f_{\vartheta\vartheta}$. Perpendicular magnetization ($\vartheta = 0$) is an energetic minimum for $t < t_{c,1}$, whereas in-plane magnetization ($\vartheta = \pi/2$) is a minimum for $t > t_{c,2}$. The nature of the transition then is determined by the ratio $t_{c,2}/t_{c,1}$, or $\sigma_{\vartheta\vartheta}(\pi/2)/\sigma_{\vartheta\vartheta}(0)$, except for hcp Co, where fourth-order volume terms become important.

We can distinguish three types of transitions:

(a) Continuous transition for $t_{c,1} < t_{c,2}$, see Fig. 2(a). In an interval $t_{c,1} < t < t_{c,2}$, both perpendicular and in-plane magnetization represent energetic maxima, with a minimum $\vartheta(t)$ between them. With increasing t, the magnetization rotates continuously from $\vartheta(t_{c,1}) = 0$ to $\vartheta(t_{c,2}) = (\pi/2)$. The anisotropy never disappears, but the easy direction rotates within the transition. This case has been observed by Allenspach, Stampanoni, and Bischof[9]

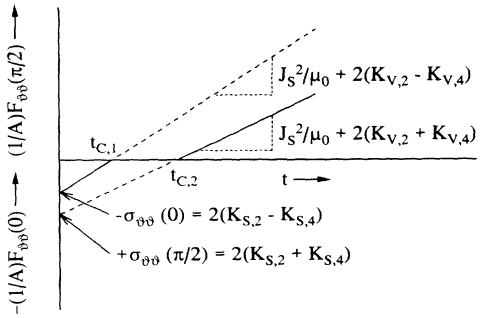

FIG. 1. Magnetic-film anisotropies per area, $F_{\vartheta\vartheta}(\vartheta)/A$, for $\vartheta = \pi/2$ and 0, respectively, versus film thickness t; see Eqs. 3(a), 3(b), 4(a), and 4(b). The quantities are given by the full lines where they are positive and therefore can be measured, e.g., by TOM.

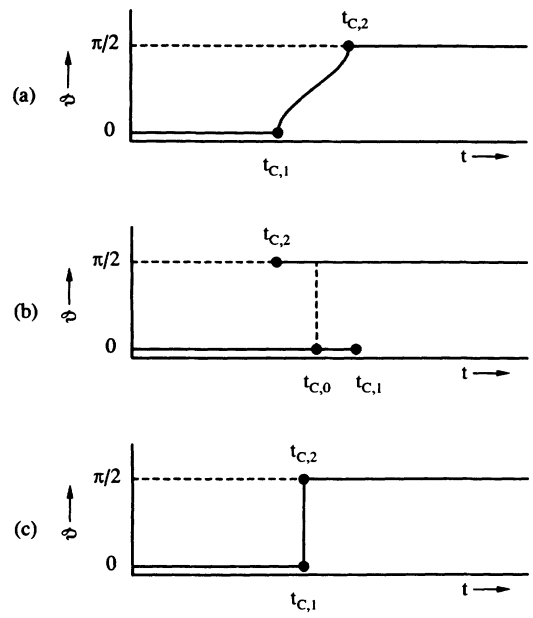

FIG. 2. Types of the spin-reorientation transition. The ranges of stability (metastability) are indicated for perpendicular magnetization ($\vartheta=0$) and in-plane magnetization ($\vartheta=\pi/2$), respectively. (a) Continuous transition with a gap between both ranges. (b) Discontinuous transition with an overlap of the ranges. (c) Special transition.

in hcp Co on Au(111) and could be explained based on fourth-order volume anisotropies.

(b) Discontinuous transition for $t_{c,1} > t_{c,2}$, see Fig. 2(b). In an interval $t_{c,2} < t < t_{c,1}$, both perpendicular and in-plane magnetization represent energetic minima, with a maximum between. The magnetization then switches between both minima at some thickness $t_{c,0}$ between $t_{c,2}$ and $t_{c,1}$ where the depths of both become equal. Again, the anisotropy does not really disappear. Hysteresis must be considered. To our knowledge, a transition of this type has not yet been reported. Transition types (a) and (b) have been mentioned by Grolier *et al.*,[21] however without reference to higher-order MSA.

(c) Special transition for $t_{c,1}=t_{c,2}$, see Fig. 2(c). The transition is of this special type in the quadratic approximation. Our experiments to be discussed below show that in real systems this can hardly be expected. Note that the special transition is the only one for which the anisotropy really disappears; it is the subject of available theories of the transition.

We determined second- and fourth-order terms of out-of-plane MSA in uncovered Fe(110) films on Cr(110) and in Pd-covered Co(111) films on Pd(111), by TOM *in situ* in UHV. For the case of Fe(110), the Cr(110) substrates consisted of 12 atomic layers thick Cr films prepared at 560 K on W(110); they showed atomically smooth surfaces, as tested by high angular resolution low-electron diffraction (SPA-LEED). Fe(110) was prepared on them at 300 K; it was pseudomorphic with the Cr substrate in the range up to 30 monolayers which were used. TOM was performed with a field in the $[1\bar{1}0]$ azimuth. The uncovered films showed perpendicular magnetization below roughly 2.5 monolayers (0.5 nm). Figure 3 shows anisotropy parameters $F_{\vartheta\vartheta}(\pi/2)$ and $F_{\vartheta\vartheta}(0)$, respectively, versus Fe-film thickness t, which can be evaluated as shown in Eqs. 3(a), 3(b), 4(a), and 4(b) and in Fig. 1. The difference in the axial sections indicates a finite fourth-order surface anisotropy. Numerical evaluation results in $K_{S,2}=(-1.06\pm0.05)$ mJ/m^2 and $K_{S,4}=(-0.09\pm0.05)$ mJ/m^2. The difference between $t_{c,1}=(0.55\pm0.08)$ nm and $t_{c,2}=(0.71\pm0.04)$ nm shows that the transition is continuous. An evaluation of the slopes results in $K_{V,4}=(-6.5\pm9)\times10^4$ J/m^3, in agreement with an expectation $K_{V,4}=-K_1=-4.8\times10^4$ J/m^3. The second-order volume term $K_{V,2}=(-16.2\pm9)\times10^4$ J/m^3 can be explained as a strain anisotropy with an in-plane strain $\varepsilon=0.0123$, slightly larger than the magnitude of the misfit to a tentative bulk Cr substrate, $f_{\mathrm{FeCr}}=-0.007$. This enlarged strain can be explained with the reasonable assumption that the 12 layers Cr substrate itself forms a coincidence structure with the W(110) substrate with a slightly strained $a^*_{\mathrm{Cr}}=(11/12)a_{\mathrm{W}}=1.006a_{\mathrm{Cr}}$. The reasonable values of volume anisotropies provide further support on the validity of the surface anisotropy analysis in particular on the existence of a nonvanishing $K_{S,4}$ and a difference between $t_{c,1}$ and $t_{c,2}$.

The second experimental example is given by Pd-covered Co films on Pd(111). Perpendicular magnetization and perpendicular MSA in Pd/Co/Pd(111) samples has been reported by several groups.[10–12] We prepared Co films on 12 atomic layers thick Pd(111) films which in turn were prepared by epitaxy on W(110) at 300 K and annealed at 600 K. The Pd substrates showed sharp LEED patterns. Co films were prepared on them at 300 K and covered with Pd at 300 K. TOM was performed with the field in the [001] azimuth. For a series of such samples of type Pd(111)/Co/Pd, with Co thickness t_{Co} between 0.4 and 2.5 nm (2 to 13 monolayers), the anisotropies are shown in Fig. 4. The slopes of $F_{\vartheta\vartheta}(\pi/2)/A$ and $F_{\vartheta\vartheta}(0)/A$ result in $K_{V,2}=-4.4\times10^5$ J/m^3, in fair agreement with an expectation $K_{V,2}=-K_1-K_2=-5.1\times10^5$ J/m^3. They further result in a surprisingly large value of $K_{V,4}=+3.5\times10^5$ J/m^3. The difference of the axial sections again shows a nonvanishing fourth-

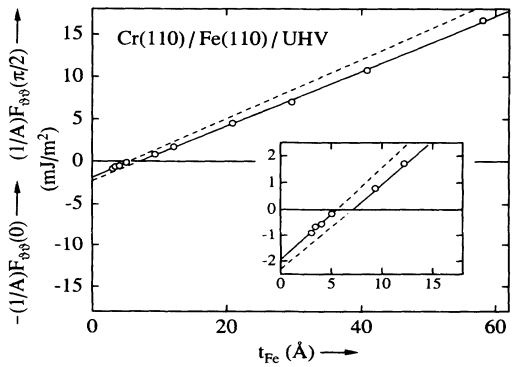

FIG. 3. Anisotropies of uncovered Fe(110) films on Cr(110), represented as in Fig. 1.

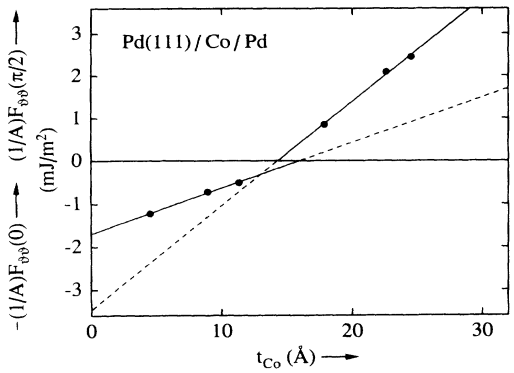

FIG. 4. Anisotropies of Pd-covered Co films on Pd(111), represented as in Fig. 1.

order surface anisotropy. For the present symmetrical sandwich, we can determine single interface anisotropies of the Pd/Co interface, which finally result as $K_{S,2}^{CoPd}=(-0.65+0.05)$ mJ/m^2 and $K_{S,4}^{CoPd}=(-0.22\pm0.05)$ mJ/m^2. Our result for $K_{S,2}^{CoPd}$ is in agreement with results of den Broeder, Hoving, and Bloemen[12] for epitaxial Co/Pd multilayers, $K_{S,2}^{CoPd}=-0.58$ mJ/m^2; because these data were obtained from the integration of hard axis loops, they represent the energetic difference between perpendicular and in-plane magnetization, that means just $K_{V,2}t+K_{S,2}$. In contrast, our result differs from the value reported by Purcell *et al.*[11] as a result from Pd/Co/Pd sandwiches on Pd(111) single crystals, $K_{S,2}^{CoPd}=-0.92$ mJ/m^2; however, careful inspection of this work shows that, using Kerr magnetometry in a special geometry, the authors actually measured some combination of $K_{S,2}$ and $K_{S,4}$; being unable to separate between the two, they assumed values of $K_{S,4}$ which apparently were wrong as seen from our present data, resulting in too high values of $K_{S,2}$. A reevaluation of their data is required. The small difference between $t_{c,1}=(1.56\pm0.1)$ nm and $t_{c,2}=(1.40\pm0.2)$ nm is within the error limits. The transition is very near the special type. Note that this approximate equality of $t_{c,1}$ and $t_{c,2}$ results from a curious compensation of fourth-order surface and volume anisotropy terms.

In conclusion, we have determined nonvanishing fourth-order terms of out-of-plane MSA, for uncovered Fe(110) films on Cr(110) and for Pd-covered Co films on Pd(111). These higher-order terms of MSA, which have been neglected so far, determine the nature of the spin-reorientation transition in an elementary manner. Being aware of their presence in one particular case, one has to consider their existence in general. They must be included in any forthcoming discussion of the spin-reorientation transition. A theoretical model of these higher-order terms beyond their phenomenological description is not available.

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