

Composition-driven spin-reorientation transition in ferromagnetic alloy films

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A spin-reorientation transition upon a variation of the Fe concentration x is observed in ultrathin fcc $\text{Fe}_x\text{Co}_{1-x}$ alloy films on Cu(001) for $x > 77\%$. For film thicknesses below 4 monolayers the magnetic easy axis changes from in-plane on the Co-rich side to out-of-plane on the Fe-rich side. Since no structural transitions accompany this spin-reorientation transition, varying the alloy composition can be interpreted as varying the number of $3d$ electrons. Upon changing the average d -band filling by as little as 0.1 electron strong changes of the anisotropy energy are observed. [S0163-1829(98)51306-9]

One of the most important issues in ultrathin film magnetism is to understand the origin of the magnetic anisotropy, which determines the direction of the magnetization easy axis in ferromagnetic thin films. Because of technologically relevant applications for both magnetic thin films with a magnetization in the film plane or perpendicular to it, much experimental¹⁻¹⁰ and theoretical¹¹⁻¹⁵ effort has been dedicated to the investigation of the fundamental mechanisms ruling the anisotropy in these systems. Special contributions being connected to the presence of a surface or interface, to elastic strain, or other characteristic structural features, may become important in thin films.^{1,16} A perpendicular magnetization is observed if the resulting spin-orbit based anisotropy favors an out-of-plane orientation, and overcomes the magnetostatic demagnetizing energy, which tries to align the magnetization to the film plane. In that case spin-reorientation transitions (SRT's) from in-plane to out-of-plane as a function of film thickness or temperature occur.^{2-4,6-8} They appear at the thicknesses or temperatures at which the anisotropy energy and the demagnetizing field compensate each other.

Up to now the phenomenon of SRT has been experimentally investigated only in single-component ferromagnetic thin films. For the technologically more relevant ferromagnetic alloy films, to our knowledge no such effect has been reported up to now. In particular, the role of alloy composition, which can strongly influence electronic, magnetic, and structural properties, the anisotropy and the SRT has not been examined. This brings us to the crucial question: Can an SRT be affected or even induced by varying the relative concentration of the two constituents in a binary alloy?

Theoretical calculations of the magnetic anisotropy are usually based on the underlying electronic structure of the film, and must include all details of the film structure. Results for unstrained fcc FeCo alloy thin films with the Cu lattice parameter resulted in an in-plane orientation of the magnetization for all compositions, but indicated a strong dependence of the anisotropy energy on the Fe concentration.¹¹ Thin film anisotropies in $3d$ transition metals have been calculated as a function of the number of d holes.¹²⁻¹⁴ There has been some dispute as to how the band energies should be computed.^{13,17,18} Different methods yielded either a rather complicated dependence of the anisotropy energy on the number of d holes with rapid oscillations

(“blind band filling”¹²), or a smoother behavior (“state tracking”¹³). It has been argued in favor of the former that upon alloying Ni with only a few percent of nonmagnetic impurities, experimental anisotropy energies already change drastically.¹⁷ This has been objected by pointing out that in these systems not only the number of d holes is modified, but that there is also a strong change in magnetic moment and hence in magnetostatic energy.¹⁸ No experimental evidence for the dependence of magnetic thin film anisotropy upon the number of d holes exists to date, to our knowledge.

Here we present a study of the orientation of the magnetic easy axis in ferromagnetic alloy films as a function of composition. Using FeCo/Cu(100), it is shown that in this system an SRT occurs not only as a function of thickness and temperature—as found previously in single component films—but also as a function of alloy composition. This SRT is solely due to changes in the stoichiometry, and is not accompanied by structural transitions. Varying the composition of the chemically disordered FeCo alloy films is thus an ideal means to alter the average number of d holes, having at the same time a fixed structural arrangement of the atoms. Upon increasing the d -electron count, a strong decrease of the anisotropy energy is observed.

The magnetic anisotropies of both constituents, grown individually on Cu(001), fcc Fe (Refs. 5-7), and fcc Co (Refs. 9,10,19) have been extensively studied and can serve as a reference. Fcc Fe on Cu(001) exhibits an out-of-plane magnetization in a certain thickness range,^{3-7,20} whereas fcc Co/Cu(001) is magnetized in-plane for all thicknesses.^{9,10,19} A concentration-dependent reorientation transition may therefore be expected in fcc FeCo films on Cu(001), which was one reason to choose that system. Structural, magnetic, and electronic properties of FeCo/Cu(001) have been investigated previously.^{21,22} In short, the films grow in a pseudomorphic fcc phase on Cu(100) over the entire range of thicknesses and compositions investigated and form a chemically random alloy.²¹ The films of interest here, i.e., Fe concentrations $x > 70\%$ and film thicknesses $t < 4$ monolayers (ML), exhibit epitaxial layer-by-layer growth,²¹ and are tetragonally expanded along the surface normal relative to the Cu lattice spacing, with a constant value of $c/a \approx 1.04$.²¹ This is essentially the same as for pure Fe/Cu(001) films of 2-4 ML thickness.^{20,23} No structural change was observed upon varia-

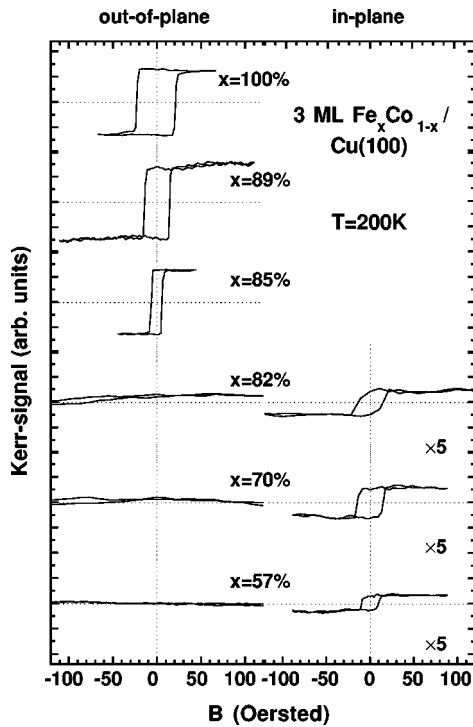


FIG. 1. Hysteresis loops in out-of-plane and in-plane geometry for $\text{Fe}_x\text{Co}_{1-x}$ films of 3 ML thickness and different x at 200 K. A spin-reorientation transition from out-of-plane to in-plane occurs between $x = 82\%$ and $x = 85\%$.

tion of either composition or thickness in the range mentioned above. From magneto-optical Kerr effect (MOKE) measurements we found evidence for a linear dependence of the magnetic moment of the alloy films in going from Fe to Co.²¹

The FeCo films were deposited at room temperature^{21,22} by coevaporation from two individual sources. The growth process was monitored and controlled *in situ* by medium energy electron diffraction, which allowed adjustment of the film thickness within about 2–5%. The composition of the films was determined by Auger electron spectroscopy with an accuracy of 5%.²¹ Structural and morphological properties of the films were checked by low energy electron diffraction. MOKE measurements were performed in a temperature range between 120 and 300 K in polar and longitudinal geometry.⁸

In Fig. 1 we present a series of MOKE hysteresis loops for a constant thickness of 3 ML and varying composition at $T \approx 200$ K. Starting from pure Fe ($x = 100\%$) we find an out-of-plane magnetization with rectangular hysteresis loops down to $x \approx 85\%$. Between 85% and 82% Fe the magnetization switches into the plane of the film, and the out-of-plane direction becomes the hard axis.

The MOKE results at various thicknesses and alloy compositions are summarized in Fig. 2 in the form of a two-dimensional phase diagram. For each film of a given thickness and composition investigated, the direction of the easy axis of magnetization at room temperature is shown by full and open circles denoting out-of-plane and in-plane magnetization, respectively. The out-of-plane magnetization is only found for $x > 70\%$ and thicknesses below 4 ML. For all other thicknesses/concentrations (also those outside the plot range)

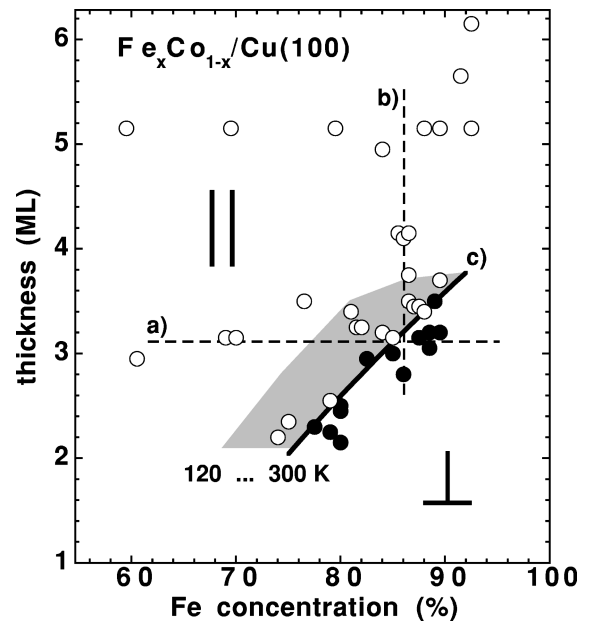


FIG. 2. Magnetic easy axis phase diagram for $\text{Fe}_x\text{Co}_{1-x}$. Open and filled circles denote in-plane and out-of plane magnetization, respectively. In the shaded region a temperature-induced spin-reorientation transition from out-of-plane at low T to in-plane at high T is observed.

an in-plane magnetization was observed. The SRT can be triggered by either varying the concentration [line (a)], the thickness [line (b)], or the temperature. In the latter case it falls within the shaded area in Fig. 2; the boundary between the regions of out-of-plane and in-plane magnetization [line (c) at room temperature] shifts to lower concentrations and higher thicknesses with decreasing temperature.

For the interpretation of the data we consider the magnetic anisotropy energy E , which is the difference of the energies for out-of-plane and in-plane magnetization, defined as positive (negative) for out-of-plane (in-plane) magnetization. As mentioned in the introduction, there are two contributions to E :

$$E = E_{dip} + E_{soc} = -\frac{1}{2} \mu_0 M_s^2 t + E_{soc}, \quad (1)$$

where E_{dip} is the magnetostatic energy, depending both on the saturation magnetization per unit volume M_s and the film thickness t ($\mu_0 = 4\pi \times 10^{-7}$ Vs A⁻¹ m⁻¹), and E_{soc} contains the remaining anisotropy energy, mainly caused by spin-orbit coupling. Both terms in Eq. (1) have the units of energy per area.

At the critical thickness [line (c) in Fig. 2] the anisotropy energy E_{soc} can be calculated by using Eq. (1), because E_{dip} and E_{soc} cancel out, which yields $E_{soc} = -E_{dip} = \frac{1}{2} \mu_0 M_s^2 t$. To do so we assumed that the average magnetic moment per atom of the alloy films decreases linearly²¹ from $2.5\mu_B$ to $1.6\mu_B$ from Fe to Co. The value of $2.5\mu_B$ corresponds to tetragonally expanded fcc Fe.²⁴ The resulting E_{soc} of the alloy films is presented in Fig. 3 as open ovals (numbers indicate Fe concentration x) together with the published values of pure Fe/Cu(001) (diamonds: Ref. 6, filled circles: Ref. 7) and Co/Cu(001) (down triangles: Ref. 9, up triangles: Ref. 10). The dashed lines are linear fits to the data for Fe and Co

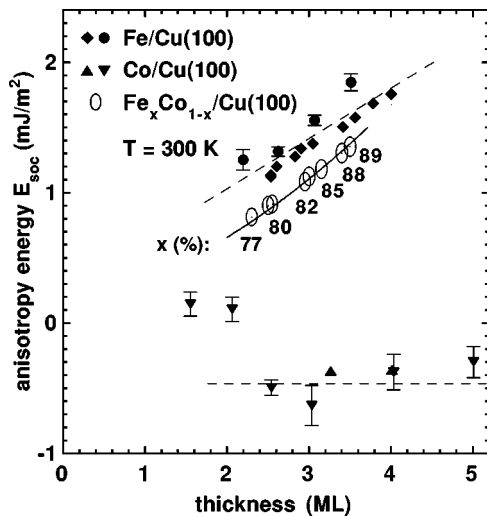


FIG. 3. Dependence of the anisotropy energy E_{soc} on the thickness for $\text{Fe}_x\text{Co}_{1-x}$ alloy films (open ovals, this paper), as well as pure Fe (diamonds: Ref. 6, filled circles: Ref. 7) and Co (up triangles: Ref. 10, down triangles: Ref. 9) on Cu(001). The values of E_{soc} in the alloy films were determined at the critical thicknesses ($T=300$ K); the corresponding Fe concentrations are indicated. Dashed lines are linear fits to the data for the single component films. The solid line represents a concentration-weighted average of these fits.

on Cu(001). The same magnetic moment of $2.5\mu_B$ has been used to convert the published Fe anisotropy fields to an energy per unit area.

To compare our data to the pure Fe and Co anisotropies we calculated an average between the fitted data for Fe/Cu(001) and Co/Cu(001), weighted by the alloy composition at the critical thicknesses. This weighted average is reproduced in Fig. 3 as a solid line. It passes through all the experimental data (ovals) for the alloy films. This suggests that at the critical thickness the anisotropy energy of the alloy films may be obtained reasonably well by a linear superposition of the anisotropy energies of the constituents, if taken from fcc films on Cu(001). We recall that the structure of the pure Fe films up to 4 ML is very similar to the one of the alloy films, with a virtually identical tetragonal expansion, while pure Co films on Cu(001) are tetragonally compressed. One may consider the agreement with the averaged pure element anisotropies accidental. However, as we are on the Fe-rich side of the phase diagram the anisotropy of pure Co enters with a relatively low weight, and does therefore not have a strong influence on the exact value of the weighted average.

Further support for our above ansatz comes, if we extrapolate our FeCo anisotropy values as a function of concentration, irrespective of the thickness. At $x=100\%$ we reach a value of 1.8 mJ/m^2 , which is in surprising accordance with the value of pure Fe/Cu(001) for a thickness of ≈ 4 ML (cf. upper dashed line in Fig. 3). Extrapolating to lower Fe concentrations, E_{soc} reaches zero around $x=60\%$. That means, assuming that the same structure is present around that composition, that below 60% Fe only in-plane magnetization should exist at all.

The data following a linear superposition of pure Fe and Co anisotropies are consistent with a smooth variation of the anisotropy energy with the band occupancy, as predicted by calculations employing the state tracking method.¹³ We must emphasize that the concentration range covered by our data corresponds to a change of only about 0.1 electron in the $3d$ band filling. Assuming this to be the exclusive origin, the corresponding increase in anisotropy energy would be about 70% of the value for $\text{Fe}_{77}\text{Co}_{23}$, namely from 0.8 to 1.35 mJ/m^2 . Together with the stoichiometry, however, also the critical film thickness for the SRT is changed from 2.3 to 3.5 ML. This change in film thickness may of course also affect the anisotropy and must be accounted for. An estimate can be based on the behavior of the anisotropy energy E_{soc} in pure Fe/Cu(100), which from 2.3 to 3.5 ML changes by about 40% (cf. upper dashed line in Fig. 3). It is reasonable to assume a similar thickness dependence for E_{soc} to hold in the FeCo alloy films with high Fe concentration. This finally leaves a more than 20% increase of the anisotropy energy due to the reduction of the d -band filling by 0.1 electron.

It is clear that a linear extrapolation of E_{soc} , as it was done above, is surely only valid for a relatively narrow range of the d -electron count. The strong dependence of the anisotropy upon variation of the band filling, which is also much stronger than the simultaneous change of the average magnetic moment, points towards a strong influence of the electronic structure at the Fermi edge, as comes out from calculations using the blind band filling method.¹² It has been shown recently by Lessard *et al.* from theoretical calculations that one of the most important contributions to the magnetic anisotropy in thin films follows from band degeneracies right at the Fermi edge which are lifted for one direction of the magnetization, if these degeneracies run along a line in \mathbf{k} space.¹⁴ Upon variation of the number of electrons in the valence band, these degeneracies shift across the Fermi edge, which may vary their impact on the anisotropy energies substantially. In Ref. 14 several important contributions of such lifted degeneracies to the anisotropy energy have been identified in the $3d$ minority spin band of Fe/Cu(001). In a rigid-band model with typical average d -band density of states of 2 (eV)^{-1} (Ref. 25) we can estimate the addition of 0.1 electron to be roughly equivalent to a band shift of about 0.05 eV for the center of the exchange split bands. Due to the simultaneous variation of the exchange splitting, minority (majority) bands are more (less) strongly shifted. The estimated shift is small, but may very well account for the observed variation in E_{soc} with alloy composition.

From the present data alone it can hardly be decided whether rapid oscillations or a smooth behavior of the anisotropy energy with d -band filling is realized in alloy ultrathin films. Our data are on the one hand consistent with a simple superposition of elemental anisotropies, but indicate on the other hand that drastic changes of the anisotropy with only small variations of the number of d electrons are possible.

In conclusion, the SRT's in fcc FeCo alloy films on Cu(001) have been investigated. In particular, a new type of SRT occurs upon changing the stoichiometry, which has not been observed previously in ferromagnetic alloy films. Since no accompanying change in film structure is observed, the influence of the alloy composition must be due to changes in

the electronic structure only. The effect is interpreted as due to shifts in the spin-split band structure upon changing the number of $3d$ electrons. The present work thus constitutes the first experimental investigation of the magnetic anisotropy in ultrathin films as a function of valence band occupancy. The alloy composition as an additional parameter to control the spin orientation in ferromagnetic alloy films offers exciting new possibilities for tailoring properties of

magnetic structures and devices based on thin-film technology.

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¹U. Gradmann, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (North-Holland, Amsterdam, 1993), Vol. 7.

²Z. Q. Qiu, J. Pearson, and S. D. Bader, *Phys. Rev. Lett.* **70**, 1006 (1993); B. Schulz and K. Baberschke, *Phys. Rev. B* **50**, 13 467 (1994).

³R. Allenspach and A. Bischof, *Phys. Rev. Lett.* **69**, 3385 (1992); J. Thomassen, F. May, B. Feldman, M. Wuttig, and H. Ibach, *ibid.* **69**, 3831 (1992).

⁴D. Li, M. Freitag, J. Pearson, Z. Q. Qiu, and S. D. Bader, *Phys. Rev. Lett.* **72**, 3112 (1994).

⁵J. F. Cochran, W. B. Muir, J. F. Rudd, B. Heinrich, Z. Celinski, T. T. Le-Tran, W. Schwarzacher, W. Bennet, and W. F. Egelhoff, Jr., *J. Appl. Phys.* **69**, 5206 (1991).

⁶P. Xhonneux and E. Courtens, *Phys. Rev. B* **46**, 556 (1992).

⁷D. E. Fowler and J. V. Barth, *Phys. Rev. B* **53**, 5563 (1996).

⁸M.-T. Lin, J. Shen, W. Kuch, H. Jenniches, M. Klaua, C. M. Schneider, and J. Kirschner, *Phys. Rev. B* **55**, 5886 (1996).

⁹M. Kowalewski, C. M. Schneider, and B. Heinrich, *Phys. Rev. B* **47**, 8748 (1993).

¹⁰P. Krams, F. Laubs, B. Hillebrands, R. L. Stamps, and G. Güntherodt, *Phys. Rev. Lett.* **69**, 3674 (1992).

¹¹J. Zabloudil, Master's thesis, Technical University of Vienna, Austria, 1997; J. Zabloudil and P. Weinberger (private communication).

¹²G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, *Phys. Rev. B* **41**, 11 919 (1990).

¹³D.-S. Wang, R. Wu, and A. J. Freeman, *Phys. Rev. Lett.* **70**, 869 (1993).

¹⁴A. Lessard, T. H. Moos, and W. Hübner, *Phys. Rev. B* **56**, 2594 (1997).

¹⁵B. Újfalussy, L. Szunyogh, and P. Weinberger, *Phys. Rev. B* **54**, 9883 (1996); L. Szunyogh, B. Újfalussy, and P. Weinberger, *ibid.* **55**, 14 392 (1997); R. Lorenz and J. Hafner, *ibid.* **54**, 15 937 (1996); A. Hucht and K. D. Usadel, *ibid.* **55**, 12 309 (1997).

¹⁶L. Néel, *J. Phys. Radium* **15**, 225 (1954).

¹⁷G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, *Phys. Rev. Lett.* **71**, 2165 (1993).

¹⁸D.-S. Wang, R. Wu, and A. J. Freeman, *Phys. Rev. Lett.* **71**, 2166 (1993).

¹⁹C. M. Schneider, A. K. Schmid, P. Schuster, H. P. Oepen, and J. Kirschner, in *Magnetism and Structure in Systems of Reduced Dimension*, edited by R. F. C. Farrow *et al.* (Plenum Press, New York, 1993).

²⁰S. Müller, P. Bayer, C. Reischl, K. Heinz, B. Feldmann, H. Zillgen, and M. Wuttig, *Phys. Rev. Lett.* **74**, 765 (1995).

²¹M. Zharnikov, A. Dittschar, W. Kuch, K. Meinel, C. M. Schneider, and J. Kirschner, *Thin Solid Films* **275**, 262 (1996); A. Dittschar, M. Zharnikov, W. Kuch, C. M. Schneider, and J. Kirschner (unpublished).

²²M. Zharnikov, A. Dittschar, W. Kuch, C. M. Schneider, and J. Kirschner, *J. Magn. Magn. Mater.* **165**, 250 (1997).

²³K. Heinz, P. Bayer, and S. Müller, *Surf. Rev. Lett.* **2**, 89 (1995).

²⁴M. Wuttig, B. Feldmann, and T. Flores, *Surf. Sci.* **331-333**, 659 (1995).

²⁵V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).