Monolayer Resolved Oscillating Hyperfine Fields in Epitaxial Face-Centered-Tetragonal Co(001) Films

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Ultrahigh-quality thin fct-Co films grown on Cu(001) have been investigated by ^{59}Co nuclear magnetic resonance. The influence of the spin-dependent electron scattering at the interfaces is observed for at least four Co atomic layers from the interface with monolayer resolution. An oscillatory effect on the Co hyperfine field with a period of several monolayers is measured, corresponding to the oscillating conduction electron polarization. The observation is exclusively possible in this system due to its very narrow resonance lines, corresponding to a virtually perfect Co structure.

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The hyperfine field of an atom in a magnetic solid is a powerful probe of the structural, magnetic, and electronic properties of the local environment. One of the most widely used methods for measuring the hyperfine field is nuclear magnetic resonance (NMR). It is particularly suited to Co-based structures [1] and of special interest for the analysis of thin Co films, which are widely used as building blocks for modern magnetoelectronic devices [2,3] and as model systems for a basic understanding of spintronic effects [4].

Although the hyperfine field is an extremely local probe of atomic-scale properties, some longer ranging influences do occur, particularly via the spin polarization of conduction electrons, which is responsible for the RKKY coupling between distant magnetic impurities and between interlayer exchange coupled magnetic layers [5]. The oscillations of the Knight shift of Cu caused by this effect have been directly observed by NMR [6,7].

The influence of foreign atoms or interfaces on the hyperfine field of magnetic atoms may also reach several atomic distances. However, the large inherent width of the Co resonance line usually obliterates these relatively small effects. Only the influence of directly neighboring foreign atoms or interfaces can usually be resolved by Co NMR [1].

The linewidth is reduced in Co films of very high structural quality, thus, for these an observation of the longer ranged effects may become feasible. A particularly suitable system is Co on Cu(001), since it is both an archetypal interlayer coupling system [8,9] and a model structure for ultrahigh-quality growth by molecular beam epitaxy (MBE) methods [10,11]. This system, combining a strong ferromagnet with a simple noble metal in a one-on-one epitaxial relationship, may be ideal for a study of a longer ranging influence of interfaces.

In this Letter we present the NMR observation of the effect of a Co/Cu interface on the Co hyperfine fields up to a few atomic distances from the interface. The effect can be resolved up to at least the fourth atomic layer in MBE grown Co films on Cu(001), and shows a small oscillation in strength with distance. This unique observation is facilitated by the virtually perfect structural quality of this system, distinctly narrowing the resonance lines in comparison to other structures. This provides a resolution of the distinct hyperfine field contributions.

The Co films were grown on Cu(001) single crystals, which were cleaned by sputter and anneal treatments until the surface was atomically flat and clean. Co was MBE grown at a sample temperature of about 50 °C and at a pressure below 10^{-10} mbar. The Co thickness was controlled by an accurately calibrated quartz-crystal microbalance. Co thicknesses above four monolayers (ML), $\sim$0.7 nm, were grown and the quality was checked *in situ* by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). *All* Co layers were then covered by 4 nm of Cu to prevent oxidation and to obtain two well-defined symmetric interfaces. The *ex situ* ^{59}Co NMR experiments were performed at 2 K in a home-built frequency-tuned spin-echo NMR spectrometer. All samples were magnetically saturated along an (in-plane) easy axis before the NMR measurements to ensure a single domain state.

The results from the LEED investigation were consistent with earlier observations [10,11], showing a face-centered tetragonal (fct) structure which is pseudomorphic with the Cu substrate. Partial strain relief sets in above about 10–15 ML thickness and the roughness is very low for all thicknesses. STM measurements show the growth to be close to layer-by-layer, but not perfectly [Fig. 1(b)]. NMR measurements on a 40 ML Co film show a single, very narrow resonance line for the bulk of the film at 215–216 MHz. This frequency corresponds to the Co fcc-phase (217 MHz), shifted slightly by the small lattice expansion caused by the strain [1]. The linewidth, usually a direct measure of the structural quality, is extremely small: the full width at half of the maximum intensity (FWHM) is only 1–2 MHz. This indicates a much better homogeneity and a smaller amount of structural defects than found in any other thin film structure measured by NMR (typically 5–10 MHz FWHM), since Co layers of this quality have not been analyzed by NMR before. The width is close to that observed for bulk single crystals (0.7–1.0 MHz FWHM) [1]. The linewidth in our films is actually not mainly due to structural defects, but to the homogeneous tetragonal distortion in the layer. This breaks the cubic symmetry and produces electric field gradients which interact with the quadrupole moment of the cobalt nucleus and effectively broaden the resonance line [12].

For Co thicknesses below 20 ML the linewidth increases strongly (up to more than 5 MHz FWHM) with decreasing thickness. Since the strain and structural quality do not significantly change, this broadening can only be attributed to an apparently larger influence of the interfaces.

To study this in more detail, a more accurate measurement of the thinnest films was performed. The resulting spectra for 6, 7, 8, 10, 12, and 15 ML Co films are plotted in Fig. 1(a). The resonance line, which from an NMR perspective is considered to correspond to Co atoms in a single environment (i.e., a homogeneously strained, fct phase with no foreign neighbor atoms), clearly deviates from the expected single Gaussian line profile.

We will now show in detail that the spectra straightforwardly point to the experimental fact that indeed distinct contributions of Co MLs at various distances from the interfaces can be distinguished. Apart from a small and very broad background (attributed to Co deposited on the sides of the Cu crystal), the 6 ML film seems to consist of *two* sublines (at about 211 and 214 MHz), although these are very much merged. The internal structure gets more clear for 8 ML and shows two lines at approximately the same positions as for the 6 ML film and a *third* line at about 216.5 MHz. For thicker layers a constantly growing *fourth* line seems to appear around 215 MHz. For a quantitative understanding of these features, spectra for 6, 7, 8, 9, 10, 11, 12 and 15 ML Co films, have been fitted (in the range of 209 to 218 MHz) with the sum of up to four Gaussian line profiles. Each spectrum can be fitted excellently by at most four lines of nearly equal width. This width (about 2 MHz FWHM) is similar to the total width for thick Co films, where the influence of the interfaces on the spectra is negligible. An example is given in Fig. 1(b), where both the raw spectrum of a 10 ML Co film and its fit are plotted.

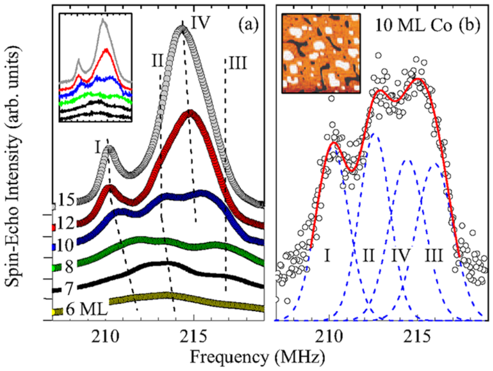

FIG. 1 (color online). (a) Smoothed NMR bulk spectra for Co layers of 15, 12, 10, 8, 7, and 6 ML thickness, respectively. The dotted lines in the graph indicate the positions at which the lines of the substructure are located. The inset shows the raw data (same scale). (b) Raw spectrum of the 10 ML film (circles) plotted together with the fit (solid line) and the four lines constituting the fit (dashed lines). The ostensible "shoulders" of the spectrum are due to the background noise in the absence of a real signal. The inset shows an STM measurement on the 10 ML Co film before Cu coverage (80×80 nm^2).

The positions of the lines vary slightly for the thinnest films only. The relative areas develop in a systematic way with film thickness. The two sublines of the 6 ML spectrum have a roughly equal area, denoted by A. Since the two Co layers that are directly at the interfaces, do not lie in this "bulk" region of the spectrum, an area of $\frac{1}{2}A$ in the spectrum corresponds to 1 ML of Co. Analysis of the 7 ML spectrum results in the same two lines, each with an area of A again, together with a third line with an area of roughly $\frac{1}{2}A$. In the 8 ML measurement, the area of this third line has increased again to A. For the 9 ML film a fourth line of area $\frac{1}{2}A$ appears and the intensity of this line doubles for the 10 ML film, which thus is built up by four lines of equal area A. For the thicker layers the intensity of this fourth line increases with an area of $\frac{1}{2}A$ for each extra ML Co.

We feel that these experimental facts show unambiguously that the different lines observed indeed correspond

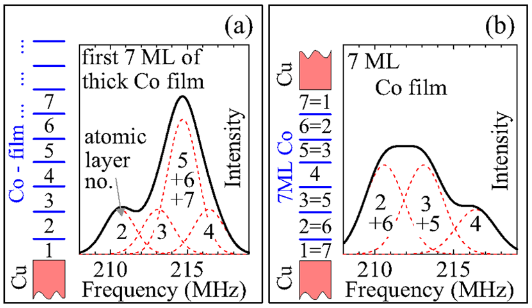

FIG. 2 (color online). The relation between a flat Cu(001)/Co film of a certain number of ML and the resulting spectrum. A single interface (a) results in different resonance lines (apart from the interface) for the second, third, and fourth layers, and for the other layers together. A simulated spectrum of the first seven Co MLs on Cu(001) in a very thick film (which is equivalent to the spectrum of a 14 ML Co film, apart from a factor of 2 in the intensity) is plotted as an example. A Cu-covered 7 ML film has two equivalent Co/Cu interfaces (b) and thus less resonance lines: since the fifth layer from the bottom is the third layer from the top, it has from symmetry reasons the same resonance frequency as the third layer (similarly for the sixth and the second layer). *Nota bene* that all experimental NMR results were obtained from Cu-covered Co films.

to Co MLs at different distances from the interface. The observable influence of the interfaces on the Co hyperfine field thus extends much further than only to the interface Co layer itself as was found until now by NMR [1]. The symmetry of the films exactly results in the measured number and intensity of the sublines for all thicknesses, as illustrated in Fig. 2.

With these considerations we can determine the hyperfine field B_{hf} of a Co layer as a function of the distance to a (001)-Cu interface, using the NMR resonance condition for Co [1]: $f = -10.054(\mathrm{MHz/T})B_{\mathrm{hf}}$. The results are plotted in Fig. 3(a). The hyperfine fields of Co atoms more than four atomic layers away from the interface do not show resolvable differences any more. The average hyperfine field of these layers is equal to that of fct-Co without any influence of interfaces. Relative to this value the influence of the interface can be determined. The second and third Co ML from the interface have smaller hyperfine fields (−2.0% and −0.8%, respectively), while the fourth ML actually has an enhanced hyperfine field (+0.7%). A very slight shift of the resonance line of Co atoms more than 4 ML from the interface when going from 10 ML to 12 ML Co, seems to indicate tiny variations in the hyperfine fields of the fifth and sixth ML (at most +0.05 and −0.2%, respectively).

Since the influence of each interface reaches at least as far as the fourth ML, the Co atoms in films thinner than 8 ML are affected by both interfaces and thus have different hyperfine fields than in the thicker layers [Figs. 3(b) and 3(c)]. The effect can be well described by a simple additive influence of both interfaces. Thus, the central layer of a 7 ML Co film [Fig. 3(b)] is the fourth ML from either interface and its hyperfine field is consequently enhanced (almost) doubly (+1.2%). This effect explains the line shift for the thinnest films [Fig. 1(a)].

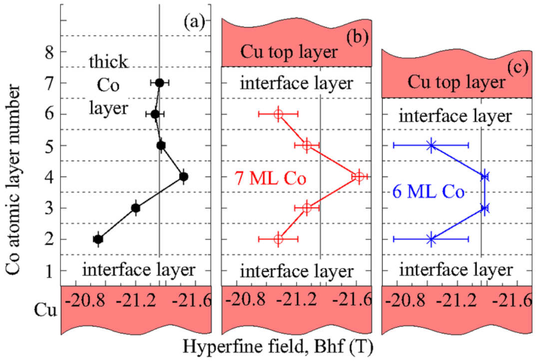

FIG. 3 (color online). Hyperfine fields versus Co ML position relative to a Co/Cu(001) interface at $T = 2$ K. (a) The influence of a single interface (as measured for at least 14 ML thick Co films). (b),(c) Co hyperfine fields within thin Co films (7 and 6 ML, respectively), where both interfaces have a significant influence on the central part of the layer. The vertical line at −21.36 T is the hyperfine field of the pure, fct-Co phase, undisturbed by the interfaces.

The assignment of the different lines to the ML position is largely straightforward and follows from the Co thickness for which they first appear. For the second and third layer this scheme does not work, however, since films thinner than 6 ML could not be measured accurately enough to provide useful information. However, the spin-spin relaxation behavior is similar for all lines except the one at 210 MHz. This behavior is known to be changed for an interface layer [1] and a smaller change may be expected for the layer next to it. Further away all layers are essentially the same and will have a similar spin-spin relaxation. Thus, the 210 MHz line can be assigned to the second Co ML. Additionally, the hyperfine fields of the 6 ML film can only be understood from an additive influence from both interfaces, if the 210 MHz line is assigned to the second Co atomic layer from the interface.

The resonance frequency of the *interface* Co layer itself, is predicted at 152 MHz (hyperfine field −15.1 T) [1,13], but experimental results are conflicting [14–16]. Our measurements do not show any interface signal (above 100 MHz) and extended tests on other Co(001) systems [12] lead us to believe that nonintermixed Co(001) interfaces are not in a straightforward way observable by spin-echo NMR. We tentatively attribute this to the Co spin-spin relaxation time, which is known to become so short for interfaces in some similar systems [17] that no spin-echo signal can be observed. In our measurements a similar effect is seen in the relaxation time of the second atomic Co layer, which is reduced by an order of magnitude compared to that of the other lines.

Having determined the hyperfine field variation per ML, we will now assess which of the several contributions to the hyperfine field is responsible for the observed variations. The hyperfine field of Co or Fe is commonly decomposed into a core, a dipole, an orbital, and a 4*s* electron field [13]. The first three terms are roughly proportional to the spin, dipole, and orbital moments of the atom itself, respectively. The influence of an interface on these moments drops off extremely rapidly with distance and is in practice mainly important for the interface layer itself. The spin moment shows large variations in some systems, but is predicted to be relatively constant in Co-Cu(001) [13,18]. It is expected to have a significant influence on the hyperfine field of the first two Co ML, but to be minor for the others. The main term having a longer ranged effect is the 4*s*-conduction electron contribution. This is determined by the conduction electron spin-density which shows Friedel oscillations at some distance to an interface (or impurity). The (spin-dependent) electron scattering at the interface causes a polarization of the conduction electrons which oscillates as a function of the distance to the interface with a period related to the extremal vectors of the Fermi surface [8]. This effect leads to oscillating interlayer exchange coupling between magnetic layers separated by a nonmagnetic metal and to RKKY coupling between magnetic impurities [5].

Just as these conduction electron polarization oscillations in a *nonmagnetic* material can be measured directly by NMR [6,7], we observe a similar oscillation within the ferromagnetic layer itself. Although we can only resolve the hyperfine field variation for the second to fifth Co MLs (and have an indication of the effect on the sixth), we still can make an estimate of the oscillation period. By fitting the hyperfine field as a function of the distance from the interface with a sine function divided by the distance squared, meanwhile taking into account that especially the second ML from the interface may still be significantly influenced by other effects than the conduction electron polarization, we find an oscillation period of 3.4 ± 0.3 ML and a phase of effectively zero. The period depends only slightly on the power used for the distance dependence and does indeed result in a slight decrease (with the right order of magnitude) of the hyperfine field for the sixth ML from the interface.

Theoretically, the period is determined by the extremal wave vectors of the Fermi surface [5] of, in our case, Co. The predicted and measured period of the interlayer coupling vs Co thickness in a Co/Cu(001) multilayer [19,20] of 3.5 ML, which should depend in the same way on the Fermi wave vectors, does indeed agree surprisingly well with our results. The strength of the effect (0.5 T for the second ML) is comparable to the induced hyperfine fields in Cu by an Fe interface (0.6 T for the second ML [7,21]), which is caused by the same mechanism and is expected to be of a similar order of magnitude.

Mössbauer spectroscopy, used as a local probe technique, has also shown the influence of an interface over several atomic layers in a magnetic material [22,23]. An oscillating hyperfine field variation for Fe(110) surfaces and a monotonously increasing hyperfine field towards an Fe(110)/Ag interface were found. Since then the technique has been applied to other Fe interfaces [24,25]. The Fe hyperfine fields reported show either a monotonic variation or a 2-ML period oscillation. Longer periods have not been reported. This may be due to the strong effect of the varying magnetic moment of Fe, which hides other influences on the hyperfine field. Moreover, Mössbauer spectroscopy is not suitable for all materials and the archetypal interlayer coupling system, Co/Cu, cannot be investigated with it.

A tool for directly obtaining local magnetic moments is x-ray magnetic circular dichroism (XMCD) [26]. It allows the separation of orbital and spin moments, but is not very sensitive to 4*s* moments and not layer resolved. NMR may thus complement XMCD results.

The reason that the conduction electron spin-polarization oscillations in Co have not been observed before lies in the relatively large linewidth in thin Co films [1]. Local probe techniques are not feasible for Co, thus the lines must be narrow enough to be resolvable. In Co on a Cu(001) single crystal the linewidth is near the achievable minimum. The extra width compared to bulk fcc Co is caused by the quadrupole splitting induced by the homogeneous strain in the layer and not by other common broadening effects (inhomogeneous strain, grain boundaries, dislocations, and growth faults). The spectra clearly indicate that any extra linewidth (as obtained, e.g., by using Cu buffer layers instead of single crystals) would merge the sublines beyond recognition.

In conclusion, we have observed and resolved the effect of an interface on the Co hyperfine field in Co/Cu(001) over a distance of at least 4 ML. The hyperfine field follows mainly the Friedel oscillation of the conduction electron polarization within the Co layer. The oscillation period of 3.4 ± 0.3 ML corresponds to the value expected from the extremal wave vectors in the Co minority spin Fermi surface. The effect is resolvable only, thanks to the ultrahigh quality of the epitaxial Co/Cu(001) systems used, which results in ideally narrow NMR lines.

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[1] P. C. Riedi, T. Thomson, and G. J. Tomka, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1999), Vol. 12, pp. 97–258.

[2] P. LeClair *et al.*, Phys. Rev. Lett. **88**, 107201 (2002).

[3] E. B. Myers *et al.*, Science **285**, 867 (1999).

[4] S. A. Wolf *et al.*, Science **294**, 1488 (2001).

[5] A. Fert and P. Bruno, in *Ultrathin Magnetic Structures II*, edited by B. Heinrich and J. A. C. Bland (Springer-Verlag, Berlin, 1994), pp. 82–116.

[6] D. V. Lang *et al.*, Phys. Rev. B **9**, 3077 (1974).

[7] Q. Y. Jin *et al.*, Phys. Rev. Lett. **72**, 768 (1994).

[8] P. Bruno and C. Chappert, Phys. Rev. Lett. **67**, 1602 (1991).

[9] J. J. de Vries *et al.*, Phys. Rev. Lett. **75**, 4306 (1995).

[10] W. Weber *et al.*, Phys. Rev. B **54**, 4075 (1996).

[11] E. Navas *et al.*, J. Magn. Magn. Mater. **121**, 65 (1993).

[12] H. Wieldraaijer, W. J. M. de Jonge, and J. T. Kohlhepp (to be published).

[13] G. Y. Guo and H. Ebert, Phys. Rev. B **53**, 2492 (1996).

[14] Y. Suzuki, T. Katayama, and H. Yasuoka, J. Magn. Magn. Mater. **104–107**, 1843 (1992).

[15] T. Thomson *et al.*, J. Magn. Magn. Mater. **156**, 89 (1996).

[16] J. C. Lodder *et al.*, J. Magn. Magn. Mater. **118**, 248 (1992).

[17] G. J. Strijkers *et al.*, Appl. Magn. Reson. **19**, 461 (2000).

[18] L. Szunyogh *et al.*, Phys. Rev. B **56**, 14036 (1997).

[19] P. Bruno, Europhys. Lett. **23**, 615 (1993).

[20] P. J. H. Bloemen *et al.*, Phys. Rev. Lett. **72**, 764 (1994).

[21] B. Drittler *et al.*, Phys. Rev. B **39**, 6334 (1989).

[22] S. Ohnishi, M. Weinert, and A. J. Freeman, Phys. Rev. B **30**, 36 (1984).

[23] J. Korecki and U. Gradmann, Europhys. Lett. **2**, 651 (1986).

[24] G. Liu and U. Gradmann, J. Magn. Magn. Mater. **118**, 99 (1993).

[25] J. Zukrowski *et al.*, J. Magn. Magn. Mater. **145**, 57 (1995).

[26] P. Srivastava *et al.*, Phys. Rev. B **58**, 5701 (1998).