Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Magnetism and Magnetic Materials 285 (2005) 95–100
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Oscillatory Curie temperature in ultrathin ferromagnets: experimental evidence

C. Rüdt*, A. Scherz, K. Baberschke

Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

Received 12 May 2004; received in revised form 13 July 2004
Available online 27 August 2004

Abstract

We determined the Curie temperature T_C for 2–3 monolayers of Co/Cu(1 0 0) as a function of Cu-cap thickness by means of temperature-dependent measurements of the initial zero-field AC susceptibility. We see a strong reduction of T_C that we discuss in terms of hybridization effects and modifications of the electronic structure of Cu. In addition, we found a small oscillatory contribution that reflects an indirect exchange interaction J_{cap} in the ultrathin Co films mediated by quantum-well states in the nonmagnetic Cu overlayer. We estimate that J_{cap} is of the order of 2 μeV/atom which corresponds to an oscillation amplitude of 4 K as observed in our experiment.

PACS: 68.35.Rh; 73.63.Hs; 75.40.Cx; 75.70.−i

Keywords: Phase transitions; Quantum-wells; Susceptibility; Thin films

1. Introduction

The Curie temperature T_C of low-dimensional ferromagnets (FM) can be tailored via finite-size effects, magnetic anisotropies as well as by the indirect interlayer exchange coupling (IEC) in magnetic multilayers which is of importance not only for fundamental research but also for technological applications [1–5]. Hereby, T_C is lowered approaching the ultrathin film limit from bulk-like ferromagnets due to the confinement of the correlation length in the third dimension, and can be further reduced by hybridization at non-magnetic protective overlayers. Conversely, IEC in multilayers raises the ordering temperature of magnetic sublayers due to an effective suppression of enhanced spin-fluctuations in 2D-like ferromagnets. The Curie temperature T_C is intrinsically described by the direct exchange coupling, the spin moment and the coordination number of the magnetic ensemble. In this Letter, we present the experimental proof for an indirect exchange

*Corresponding author. Tel.: +49-30-8385-6143; fax: +49-30-8385-3646.
E-mail address: babgroup@physik.fu-berlin.de (C. Rüdt).

0304-8853/$ - see front matter
doi:10.1016/j.jmmm.2004.07.021

interaction in an ultrathin itinerant ferromagnet which is mediated by quantum-well (QW) states in a nonmagnetic capping-layer. This Ruderman–Kittel–Kasuya–Yoshida (RKKY) type of exchange interaction leads to an oscillatory behavior of T_C. This effect has been predicted theoretically by Pajda et al. [6], stimulated by an experimental work of Vollmer et al. [7]. On the basis of the present work we will clarify the existence of an oscillating T_C which was controversially discussed in literature [6–8]. In this Letter, we will discuss the influence of cap layers on the Curie temperature of ultrathin films. Hereby, we constitute three different contributions changing T_C in our experiments: a drop of T_C due to a change in the magnetic moment at the FM/cap interface, a further monotonic decrease of T_C with increasing Cu coverage caused by changes of the electronic structure of the Cu cap towards bulk, and an oscillatory behavior of the Curie temperature due to the electron confinement in the Cu overlayer. For the latter, we give an estimate of the indirect exchange interaction.

2. Experimental details

The oscillation of T_C is a rather small effect, hardly observable using conventional magnetometry which is usually sensitive to the expectation value $\langle \boldsymbol{S}_z \rangle$. In contrast, due to its proportionality to $\langle \boldsymbol{S}^2 \rangle$ the susceptibility is a powerful tool to determine T_C at the phase transition in a direct and very precise manner [9,10]. In our experimental setup both the real $\chi'(T)$ and the imaginary part $\chi''(T)$ of the complex quasistatic AC susceptibility $\chi(T) = \chi'(T) + i\chi''(T)$ are measured in an oscillatory magnetic field $H(t) = \hat{H}\cos(\omega_0 t)$ using a classical mutual inductance (MI) bridge [11]. Here, $\chi(T)$ is directly proportional to the difference between the induction signals of two identical secondary coils with and without the sample. Using a paramagnetic substance of well-known susceptibility $\chi(T)$ is calibrated in SI units. For the measurements reported here, $\chi'(T)$ and $\chi''(T)$ were simultaneously recorded at fixed excitation frequency $\nu_0 = 213\,\mathrm{Hz}$ and modulation amplitude $\hat{H} = 70\,\mathrm{mOe}$ and $\hat{H} = 140\,\mathrm{mOe}$, respectively, using lock-in technique. For $Cu_d/Co_{2-3}/Cu(1\,0\,0)$ $H(t)$ was applied along the in-plane Co[1 1 0] easy axis. Remaining static laboratory fields, like, e.g., the earth-magnetic field, were compensated with sufficient accuracy, i.e. better than 10 mOe using a pair of calibrated Helmholtz coils. Low-temperature rates of 3–5 mK/s were used in order to measure the proper initial zero-field susceptibility. The temperature resolution is 50 mK.

All measurements were performed in situ in ultrahigh vacuum with a base pressure of 4×10^{-11} mbar. As substrate a Cu(1 0 0) single crystal was used. The crystal was cleaned by several cycles of Ar^+ sputtering and subsequent annealing up to 850 K for 10 min as long as no contamination was detected via Auger electron spectroscopy (AES) and sharp low-energy electron diffraction spots were observed. The Co films were deposited at $T = 300\,\mathrm{K}$ by e-beam evaporation. During evaporation of both Co and Cu the pressure does never exceed 2×10^{-10} mbar. In order to observe sizable T_C oscillations, 1 ML of Co would be the best choice, since the effect is expected to be most pronounced the thinner the ultrathin films are. However, below 1.8 ML the magnetic and structural properties of Co/Cu(1 0 0) are notoriously difficult, see e.g. [12,13]. Hence, a thicker Co coverage slightly above 1.8 ML was chosen. Therefore, 2.2 ML and 2.5 ML films of Co were prepared having their Curie temperatures in a convenient temperature range for our experimental setup (in order to achieve low-temperature rates of mK/s). Then the films were covered successively with Cu, and T_C was measured step by step as a function of the cap thickness d. In this work two series for this type of system with Cu cap thicknesses $1\,\mathrm{ML} \leqslant d \leqslant 6\,\mathrm{ML}$ were investigated. The Co and Cu thickness was calibrated via a Quartz microbalance and AES.

3. Results and discussion

The results for the two Co series are shown in Fig. 1. First of all, the Curie temperatures of the uncapped Co films agree very well with the well-known finite-size law obtained by several groups [12,14,15]. We find that capping of the ultrathin

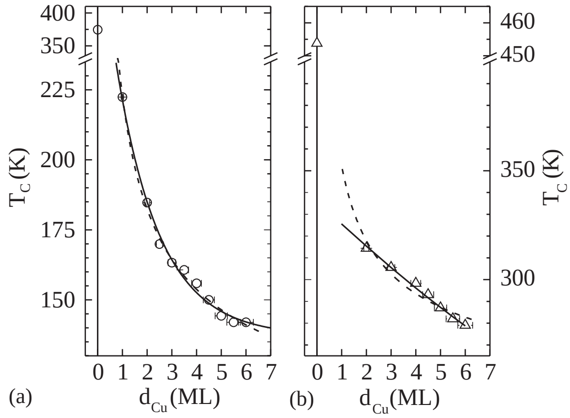

Fig. 1. Curie temperature T_C as function of the Cu cap thickness d for (a) $Cu_d/Co_{2.2}/Cu(1\,0\,0)$ (circles) and (b) $Cu_d/Co_{2.5}/Cu(1\,0\,0)$ (triangles). The solid and dashed lines are background functions as explained in the text.

films results in three different effects: (i) the drastic drop of T_C for $d = 1$ ML Cu, (ii) the continuous and monotonic decrease of T_C towards higher coverages and (iii) an oscillatory contribution which can clearly be seen. We start the discussion with (i) and (ii). The drop of T_C for the 2.2 ML Co (2.5 ML Co) film is of the order of 150 K (100 K). This effect arises from hybridization at the common interface between Co and Cu [16]. Recent SQUID [17] and XMCD measurements [16] have determined a layer-resolved profile for Co films on Cu(1 0 0) yielding an enhancement of the magnetic moment at the Co/vacuum interface (+32%) and a reduction at the Co/substrate interface (−17%) relative to the inner layers. The Cu overlayer thus dramatically changes the magnetic moment of the topmost Co layer. The resulting overall reduction in the magnetic moment for 2 ML of Co by a Cu cap amounts to ≈ 23%. This means accordingly that the drop of T_C is mainly caused by the change of the magnetic moment at the interface since T_C is proportional to μ^2. Within a simple estimate one calculates a reduction in T_C from 370 K to 220 K for 1 ML of Cu which is in reasonable agreement with our data, see Fig. 1(a). This change appears to be less pronounced for the thicker 2.5 ML Co film where T_C is expected to drop down to 300 K. Although one may intuitively expect that for higher coverages the Curie temperature of the Co film stays unaffected, we observe a continuous and monotonic decrease of T_C. This suggests that not only hybridization phenomena at the interface but also the modification of the electronic structure of the Cu cap with increasing thickness influence the T_C of the underlying ferromagnetic film. Indeed, angle-resolved-photoemission data by Johnson et al. [18] for $Cu_{2-8}/Co_{20}/Cu(1\,0\,0)$ show a large enhancement of the effective mass of QW states in the thinner Cu films. It turns out that only above 8 ML of Cu the electronic structure corresponds to the one of Cu bulk. In addition, interdiffusion [19] may contribute to the monotonic decrease of T_C. On the other hand, demixing of Co and Cu atoms at the interface was observed for this system; in any case all this may modify the monotonic change of T_C but not the oscillatory behavior.

We now come to (iii), i.e. the oscillatory behavior of the Curie temperature which appears to be the smallest contribution in Fig. 1. For the analysis of the oscillatory part one needs to subtract the monotonic background (ii). Since, to our knowledge, theoretical investigations for this effect are not performed so far, we have assumed two model functions for the thickness dependence of T_C: an exponential-like behavior $\propto \exp(-\lambda d_{Cu})$ (solid line) and a power law $\propto d_{Cu}^{-\zeta}$ (dashed). In case of the 2.2 ML Co film, Fig. 1(a), we obtained an exponent ζ close to 0.5. This suggests that the monotonic decrease of T_C is rather related to the change of the electronic structure than solely to the interface. The background can be reasonably well described by an exponential law, too. On the other hand, a proper depiction of the data is more difficult for 2.5 ML Co, Fig. 1(b). Here, an exponential background function better fits the data than a power law with $\zeta = 0.5$ (dashed line). The outcome ΔT_C by subtraction of the exponential background function is presented in Fig. 2 for both the series $Cu_d/Co_{2.2}/Cu(1\,0\,0)$ (circles) and $Cu_d/Co_{2.5}/Cu(1\,0\,0)$ (triangles). Obviously, the experimental data for 2.2 ML of Co reveal a small but significant oscillation of ≈ ±4 K in the investigated thickness range. Note, that the period of this oscillation is not affected by using the alternative power-law background whereas amplitude and phase may vary slightly within the error bar. Furthermore, we find the same period for the 2.5 ML Co film.

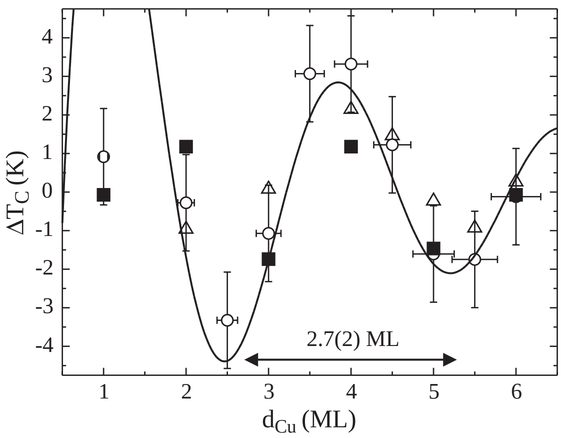

Fig. 2. Oscillations ΔT_C as a function of the Cu cap thickness d after removal of a monotonic background function, see text. Calculated values [6] are plotted for comparison (solid squares). Note that the amplitude is scaled down and the phase is shifted by $(-\pi)$ in order to match the experimental data (open symbols). According to Eq. (1) the solid line represents a damped sinusoidal function with a short period of $\Lambda = 2.7(2)$ ML.

The origin of the observed oscillations ΔT_C is the same that leads to the oscillatory behavior of the IEC with variation of the Cu cap thickness in coupled Cu/Co/Cu/Co/Cu(1 0 0) [20] and Cu/Ni/Cu/Ni/Cu(1 0 0) [21]. Due to the electron confinement in the cap layer the reflectivity at the Cu/vacuum interface varies as a function of the cap thickness d. The oscillatory Curie temperature ΔT_C can thus be reasonably well described by a damped sinusoidal function

$$\Delta T_C(d) = \frac{A}{d} \sin\left(\frac{2\pi}{\Lambda} d + \Phi\right), \qquad (1)$$

with period length $\Lambda = 2.7(2)$ ML, phase $\Phi = -1.2(4) \approx -\pi/2$ and amplitude $A = 11(2)$. The value of Λ is in excellent agreement with the well-known calculated value for the short period $\Lambda_1 = 2.56$ ML of the IEC for Cu(1 0 0). Unfortunately, the period and the phase of the calculated T_C oscillation is not provided by theory for a direct comparison. Hence, we included the theoretical data (solid squares) from Ref. [6] in Fig. 2 and rescaled the amplitude. The phase was shifted by $(-\pi)$ in order to match our experimental data. In comparison with the phase of the short period $\Phi_1 = \pi/2$ in a Cu spacer [5,22] the same phase shift $(-\pi)$ is obtained. This is most likely related to different boundary conditions, i.e. the Co thickness and imperfections of the Co/Cu and Cu/vacuum interfaces with respect to theory. In Fig. 2 we have used an envelope function $1/d$ which better fits to our experimental data. For the small thickness range shown here a $1/d^2$ function dependence would also agree with the data.

Finally, we discuss the magnitude of the oscillatory effect on the Curie temperature and give an estimate for the corresponding strength of the indirect exchange interaction mediated by the quantum-well states in the Cu cap layer for the present case. Theory predicts 20 times larger T_C oscillations for a Co monolayer than observed in our experiment, where ΔT_C amounts to a few K only for >2 ferromagnetic Co layers. The variation of T_C via an indirect exchange interaction depends, however, crucially on the thickness of the ferromagnetic layer [23,24] and it may already explain the large discrepancy. On the other hand, imperfections at the film interfaces can further reduce the amplitude of the oscillations. For an estimate of the indirect coupling strength J_{cap} we compare ΔT_C with the T_C shifts which were investigated in indirect exchange coupled Co/Cu/Ni/Cu(0 0 1) trilayers. In the thickness range from 2 to 3 ML of Ni the critical temperature is raised up to 100 K upon the IEC which suppresses the spin fluctuations of the Ni sublayer [24]. The value of $J_{inter}(d_{Cu} = 2.5\,\text{ML}) \approx 50\,\mu\text{eV/atom}$ was independently and absolutely determined by Ferromagnetic Resonance (FMR) (see Fig. 18 in Ref. [21]). Accordingly, we deduce $J_{cap} \approx 2\,\mu\text{eV/atom}$ for a $\Delta T_C \approx 4$ K. Albeit we roughly approximate the value of J_{cap}, this value agrees well with measurements of J_{inter} as a function of the Cu cap thickness in Cu/Ni/Cu/Ni/Cu(0 0 1) trilayers which is indeed of the order of a few μeV/atom (see Fig. 22 in Ref. [21]).

In a very interesting experiment Vollmer et al. [7] found an oscillatory-like behavior of the Curie temperature for Cu/Fe/Cu(1 0 0). The authors observed a strong decrease of T_C by 120 K for a 1 ML Cu cap whereas this reduction is partly reversed by 60 K for 2 ML of Cu. Further Cu coverages lead solely to a monotonic reduction within the temperature resolution. This effect was explained by Pajda et al. [6] in a theoretical framework of electron confinement in the Cu cap layer. However, on the basis of our results we favor the same interpretation as Vollmer et al. that "delocalized quantum-well states in the Cu overlayer are probably less important for the observed effect since we did not see any further oscillations at larger Cu thickness". The observed behavior for the first Cu layers is most likely due to changes in the electronic structure and hybridization effects at the interface. Hence, the interpretation of (i) and (ii) of our data is in line with Vollmer et al. In addition, we conclude from our data that the oscillatory Curie temperature (iii) is a much smaller effect compared to interface effects corroborated also by the diminutive value of J_{cap}.

4. Conclusions

In conclusion, we performed precise AC susceptibility measurements in order to accurately determine the Curie temperature T_C of Cu_d/Co/Cu(1 0 0) ultrathin films for $1\,ML \leqslant d \leqslant 6\,ML$. The T_C of Co/Cu(1 0 0) is drastically influenced by capping with Cu, resulting in mainly three different effects: (i) the drastic drop of T_C for 1 ML Cu, (ii) a continuous and monotonic decrease for higher coverages and (iii) a small oscillatory contribution which was predicted theoretically. In the case of (i) we could quantitatively demonstrate that this effect arises from a drastic change of the Co interface moment due to hybridization effects with the cap layer. In the ultrathin film limit the drop of T_C is of the order of 150 K for 2 ML of Co. (ii) We have shown that increasing Cu coverage further reduces the Curie temperature monotonously. From the thickness dependence of T_C we suggest that this phenomenon cannot solely be attributed to an interface effect. (iii) The smallest effect is the oscillatory Curie temperature which is to our knowledge observed for the first time. The period of the oscillation corresponds to the short period $\Lambda_1 = 2.56\,ML$ of the IEC for Cu(1 0 0). The phase is found to be $(-\pi/2)$. The experimental data are in good agreement with the calculations of Pajda et al. except their amplitudes. We give a reasonable estimate for the indirect exchange interaction $J_{cap} \approx 2\,\mu eV/atom$ which corresponds to the observed $\Delta T_C \approx \pm 4\,K$.

Acknowledgements

We thank P. Bruno for his continuous interest and for fruitful discussions. This work was supported by the DFG Sfb 290, TP A2.

References

[1] G. Allan, Phys. Rev. B 1 (1970) 352.
[2] R. Bergholz, U. Gradmann, J. Magn. Magn. Mater. 45 (1984) 389.
[3] C. Back, C. Würsch, D. Kerkmann, D. Pescia, Z. Phys. B 96 (1994) 1.
[4] G. Bayreuther, F. Bensch, V. Kottler, J. Appl. Phys. 79 (1996) 4509.
[5] A. Ney, F. Wilhelm, M. Farle, P. Poulopoulos, P. Srivastava, K. Baberschke, Phys. Rev. B 59 (1999) R3938.
[6] M. Pajda, J. Kudrnovský, I. Turek, V. Drchal, P. Bruno, Phys. Rev. Lett. 85 (2000) 5424.
[7] R. Vollmer, S. van Dijken, M. Schleberger, J. Kirschner, Phys. Rev. B 61 (2000) 1303.
[8] S. Razee, J. Staunton, L. Szunyogh, B. Gyorffy, Phys. Rev. Lett. 88 (2002) 147201.
[9] C. Rüdt, P. Poulopoulos, J. Lindner, A. Scherz, H. Wende, K. Baberschke, P. Blomquist, R. Wäppling, Phys. Rev. B 65 (2002) 220404(R).
[10] C. Rüdt, P. Jensen, A. Scherz, J. Lindner, P. Poulopoulos, K. Baberschke, Phys. Rev. B 69 (2003) 014419.
[11] U. Stetter, A. Aspelmeier, K. Baberschke, J. Magn. Magn. Mater. 117 (1992) 183.
[12] U. Bovensiepen, P. Poulopoulos, W. Platow, M. Farle, K. Baberschke, J. Magn. Magn. Mater. 192 (1999) L386.
[13] R. Pentcheva, M. Scheffler, Phys. Rev. B 61 (2000) 2211.
[14] C. Schneider, P. Bressler, P. Schuster, J. Kirschner, J. Miguel, R. Miranda, Phys. Rev. Lett. 64 (1990) 1059.
[15] F. Huang, M. Kief, G. Mankey, R. Willis, Phys. Rev. B 49 (1994) 3962.
[16] F. Wilhelm, U. Bovensiepen, A. Scherz, P. Poulopoulos, A. Ney, H. Wende, G. Ceballos, K. Baberschke, J. Magn. Magn. Mater. 222 (2000) 163.
[17] A. Ney, P. Poulopoulos, K. Baberschke, Europhys. Lett. 54 (2001) 820 and references therein.
[18] P. Johnson, K. Garrison, Q. Dong, N. Smith, D. Li, J. Mattson, J. Pearson, S.D. Bader, Phys. Rev. B 50 (1994) 8954.
[19] J. Fassbender, R. Allenspach, U. Dürig, Surf. Sci. 383 (1997) L742.

[20] J. de Vries, A. Schudelaro, R. Jungblut, P. Bloemen, A. Reinders, J. Kohlhepp, R. Coehoorn, W. de Jonge, Phys. Rev. Lett. 75 (1995) 4306.
[21] J. Lindner, K. Baberschke, J. Phys.: Condens. Matter 15 (2003) R193–R232.
[22] P. Bruno, C. Chappert, Phys. Rev. Lett. 67 (1991) 1602.
[23] P. Jensen, K. Bennemann, P. Poulopoulos, M. Farle, F. Wilhelm, K. Baberschke, Phys. Rev. B 60 (1999) R14994.
[24] A. Scherz, F. Wilhelm, U. Bovensiepen, P. Poulopoulos, H. Wende, K. Baberschke, J. Magn. Magn. Mater. 236 (2000) 1.