PHYSICAL REVIEW B VOLUME 57, NUMBER 22 1 JUNE 1998-II

Exchange-induced enhancement of T_C in $Co_{1-x}(EuS)_x$ macroscopic ferrimagnets

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

A. Schirmeisen
Physics Department, McGill University, 3600 rue University, Montréal, Québec, Canada H3A 2T8

R. J. Gambino
Department of Materials Science and Engineering, State University of New York, Stony Brook, New York 11794

(Received 17 December 1997)

The temperature dependence of the magnetic-exchange behavior between the EuS and the Co phase in the macroscopic ferrimagnet $Co_{1-x}(EuS)_x$ has been studied over a wide composition range, $0.1 \leqslant x \leqslant 0.6$, using magnetooptic spectroscopy. We find a strong exchange-induced enhancement of the Curie temperature of the EuS phase for EuS concentrations $x \geqslant 0.2$ reaching a maximum of 160 K in $Co_{0.6}(EuS)_{0.4}$. This is an order of magnitude higher than in bulk EuS. The maximum enhancement takes place at the concentration where a percolation from metallic to a semiconducting behavior occurs. The results are explained by the nanometer size of the EuS crystallites, which leads to a large surface-to-volume ratio. This yields a strong exchange interaction to the Co matrix while the crystallinity of the EuS ensures a high-spin Eu^{2+} state. [S0163-1829(98)04122-8]

INTRODUCTION

Magnetic thin films are of considerable interest to the scientific community as they have a high technological potential. By artificially layering, new physical properties arise like giant magnetoresistance[1,2] and oscillatory exchange.[3] The fact that the interface plays a crucial role in producing these effects has led to the investigation of phase-separated systems where the interface-to-volume ratio is increased as compared to multilayers.[4] A new class of such materials has been recently found and named macroscopic ferrimagnets.[5] In these phase-separated materials two *macroscopic* magnetic phases couple antiferromagnetically across the phase boundary. They show many of the properties of ferrimagnets as, e.g., a magnetic compensation point. So far, an antiferromagnetic exchange across a phase boundary has been found in artificially layered rare-earth/transition-metal systems such as Gd/Fe, Tb/Fe, and Dy/Fe multilayers.[6,7] However, in these multilayers both constituents are metallic with a high Curie temperature T_C whereas in the macroscopic ferrimagnets one phase (EuS) is a semiconductor with a very low T_C of 16.5 K. In addition, an exchange-induced enhancement of T_C in one of the components, as we have found in the macroscopic ferrimagnets, has not been observed before.

A prototype macroscopic ferrimagnet is $Co_{1-x}(EuS)_x$. For Co-rich samples, crystalline and semiconducting EuS precipitate particles of 10 nm diameter are embedded in a metallic Co matrix. For low-Co content, the Co acts as a magnetic impurity in a semiconducting EuS matrix.[8,9] The phase separation of Co and EuS was first discovered in x-ray-diffraction measurements.[10] They clearly reveal the crystalline nature of the EuS particles with a lattice constant of 5.97 Å equal to bulk EuS.[11] The (200) reflection is the strongest, as expected for randomly oriented EuS. Line broadening yields a crystallite size of approximately 10 nm by using the Scherrer equation.[12] The conductivity increases rapidly with volume-fraction Co. It can be fitted with a simple percolation model, corroborating that EuS is present as a semiconducting phase.[13]

In samples with $x \geqslant 0.3$, the magnetic moment μ is dominated by the EuS phase up to a compensation point T_{comp} and thereafter by the Co matrix. In contrast, for $x \leqslant 0.2$ the Co dominates at all temperatures. Assuming crystalline lattice constants and the bulk values $\mu = 1.72$ and $7\mu_B$ for Co and EuS, respectively, the magnetic moments should be at balance at an EuS concentration of $x = 0.2$, which is in good agreement with the above results. An antiferromagnetic exchange coupling between the two macroscopic phases is established by a different behavior of the remanent and the in-field Kerr spectra and of the Kerr hysteresis loops at different photon energies.[5] In $Co_{1-x}(EuS)_x$, the Co phase makes an approximately constant negative contribution to θ_K while the EuS phase exhibits a characteristic S-shaped signature due to the localized Eu^{2+} $4f \rightarrow 5d$ transition. In addition to the antiferromagnetic exchange interaction, all samples exhibit perpendicular magnetic anisotropy at low temperatures, although the EuS crystallites are randomly distributed.[5] At room temperature, a magneto-optic enhancement effect was found[14] leading to Kerr rotations $\theta_K = 2°$ above 4 eV.

In this paper we will discuss the exchange-induced enhancement of the Curie temperature $T_{C,\mathrm{EuS}}$ of the EuS phase in $Co_{1-x}(EuS)_x$. In a previous work[5] an increase of $T_{C,\mathrm{EuS}}$ up to 60 K had been found in one sample. A comprehensive study over a wider composition range now reveals an enhancement up to 160 K for $x = 0.4$, which is an order of magnitude higher as compared to the bulk EuS value of 16.5 K.[15] This enhancement is due to a strong antiferromagnetic exchange interaction between the nanocrystalline EuS particles and the metallic Co matrix. To our knowledge, this is the highest enhancement of T_C reported so far in the EuS magnetic semiconductor.

EXPERIMENT

Films of thickness 200 nm were prepared by electron-beam codeposition of Co and EuS at a rate of 0.3 nm s^{-1}. The vacuum system used for deposition has a base pressure of about 3×10^{-8} mbar. A liquid-nitrogen-cooled shroud was used that helped to keep the partial pressure of water low. The pressure during deposition increased to about 1.5 $\times10^{-7}$ mbar. The Co source was a conventional *e*-beam hearth. The EuS powder (purchased from Ames Laboratory) was evaporated from a tungsten hearth liner. The substrates were either glass, fused SiO_2, or silicon that were cooled to -15 °C. As the NaCl lattice constant of EuS, $a_{\rm EuS}=5.968$ Å, is much larger than $a_{\rm Co}=2.51$ Å and $c_{\rm Co}=4.07$ Å of hcp Co, the volume per formula unit is larger by a factor of 5. So, adding 10% EuS results in a volume fraction of 35% EuS. Phase separation is achieved solely by coevaporation. No further heat treatment such as annealing or quenching is needed.

Previously, a magnetic compensation point had been found[5] at 18 K in $Co_{0.7}(EuS)_{0.3}$, which is above T_C of bulk EuS, indicating an exchange-induced enhancement of the ordering temperature of the EuS phase. In order to analyze more carefully the influence of the exchange on the $T_{C,\rm EuS}$ of the EuS phase, we have studied the temperature dependence of the polar Kerr spectra and of the polar Kerr hysteresis loops of $Co_{1-x}(EuS)_x$, $0.1\leqslant x\leqslant0.6$, over a wide photon-energy range from 5 to 300 K in magnetic fields up to 2.7 T. In order to achieve a high angular resolution of 0.001° in the visible, the near-infrared, and the near-ultraviolet region, a lock-in technique in combination with a zeroing procedure is applied.[16]

Two independent methods were used in order to derive T_C of the EuS phase. (1) Polar Kerr spectra in the magnetic remanence state were taken between 5 and 300 K. The remanence state assures that ordering of the two phases is merely guided by the antiferromagnetic exchange. As long as an antiferromagnetic coupling is present, the EuS phase is ordered. This method yields only a lower limit of $T_{C,\rm EuS}$ because the disappearance of the remanence must not necessarily mean that $T_{C,\rm EuS}$ has been reached.[17] (2) The paramagnetic contribution of the EuS phase to the Kerr rotation $\theta_{\rm para}^{\rm EuS}$ was extracted from room-temperature polar Kerr hysteresis loops measured at various photon energies. By assuming a Curie-Weiss law the paramagnetic Curie temperature $\Theta_{\rm para}$ was determined. This method merely serves as a consistency check and the agreement with the first method justifies the assumptions made.

The accuracy of the magneto-optically derived compensation point has been checked by a superconducting-quantum-interference-device (SQUID) magnetometer. However, the ordering temperature of the EuS phase cannot be checked by the SQUID magnetometer as it measures only the volume magnetization and is not sensitive to individual components.

RESULTS

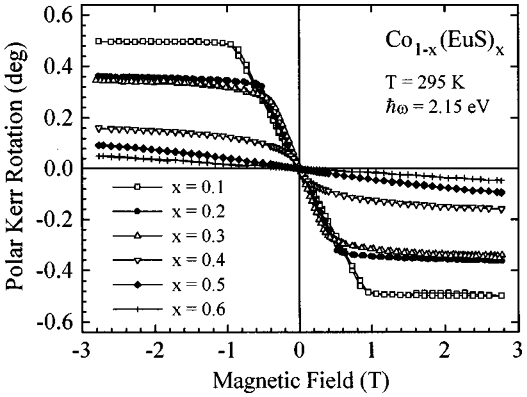

FIG. 1. Polar Kerr hysteresis loops of $Co_{1-x}(EuS)_x$ at room temperature at a photon energy of 2.15 eV.

An estimation of T_C is performed according to the second method by evaluating the high-field susceptibility of the polar Kerr hysteresis loops at room temperature. As an example, Fig. 1 shows Kerr loops at a photon energy of 2.15 eV. The loops indicate that the easy axis of the magnetization is in plane. A small high-field susceptibility is present, growing with increasing EuS concentration x. The magnetic ordering is dominated by the Co phase and at $x\geqslant0.5$ the films are paramagnetic at room temperature.

To proceed further, we make the key assumption that the magnetic moment of the Co is saturated at room temperature and shows hysteresis, while the high-field susceptibility $\chi_{\rm para}$ is solely due to the paramagnetic EuS contribution. Because of the S-shaped signature of the localized Eu^{2+} $4f\rightarrow5d$ transition, the polar Kerr loops at 2.8 and 2.15 eV comprise an EuS contribution with opposite sign while the Co contribution has the same sign and nearly the same size. Thus, by properly subtracting both loops and dividing by 2, the Co contribution cancels and we are left with the paramagnetic EuS contribution averaged between the two photon energies. A good indicator for the Co contribution to be canceled completely is the disappearance of the hysteresis in the resultant Kerr loops that is solely due to the Co. Therefore, the Kerr loop to be subtracted is multiplied by a weighting factor close to 1, which is varied until the hysteresis completely vanishes after subtraction. The result is shown in Fig. 2. Supposing a Curie-Weiss law for the EuS phase, the slope of the paramagnetic Kerr rotation $\theta_K^{\rm para}/B$ is expressed as

$$\frac{\theta_K^{\rm para}}{B}=\kappa\chi_{\rm para}=\kappa\frac{NJ(J+1)g^2\mu_B^2}{3k_B(T-\Theta_{\rm para})},\tag{1}$$

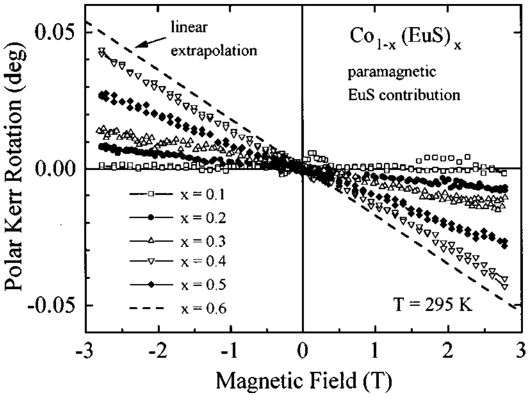

FIG. 2. Normalized difference of the room-temperature polar Kerr hysteresis loops at 2.15 and 2.8 eV corresponding to the paramagnetic Kerr rotation of the EuS phase. For $x=0.6$, the data are represented by a least-squares fit.

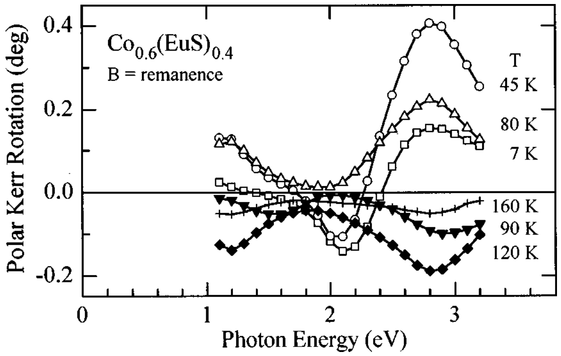

FIG. 3. Temperature dependence of the polar Kerr spectra of $Co_{0.6}(EuS)_{0.4}$ in the remanence state.

where B is the magnetic field, $J=\frac{7}{2}$ and $g=2$ for the EuS $^8S_{7/2}$ ground state, and $\kappa=\theta_K(M)/M$ is the proportionality constant between Kerr rotation $\theta_K(M)$ and magnetization M. Inserting the saturation magnetization, $M_s=NgJ\mu_B$, and using $\kappa=\theta_K(M_s)/M_s=\theta_K^{\mathrm{sat}}/M_s$, where θ_K^{sat} is obtained from the low-temperature Kerr spectra,[5] we can easily calculate Θ_{para} from the slope of the Kerr rotation,

$$\frac{\theta_K^{\mathrm{para}}}{B}=\theta_K^{\mathrm{sat}}\,\frac{(J+1)g\mu_B}{3k_B(T-\Theta_{\mathrm{para}})}. \tag{2}$$

According to the first method, θ_K has been measured in the remanence state for all samples at temperatures up to 300 K. As an example, the temperature-dependent θ_K spectra of $Co_{0.6}(EuS)_{0.4}$ are plotted in Fig. 3. The characteristic ''fingerprint'' of the EuS phase, the S-shaped feature between 2 and 3 eV, serves as an indicator of an ordered magnetic moment in the EuS phase. As long as there is an antiferromagnetic exchange, the EuS phase is still ordered yielding a lower limit to T_C. Between 80 and 90 K, a reversal of the complete spectra is observed, indicating a magnetic compensation point which is more than a factor 5 higher than T_C of bulk EuS. The S-shaped structure persists up to a temperature of 160 K.

DISCUSSION

In order to derive $T_{C,\mathrm{EuS}}$, the EuS contribution is extracted from the θ_K values at 2.8 eV (the EuS-dominated photon-energy range) and 1.1 eV (the Co-dominated part of the spectrum) as plotted in Fig. 4. The extraction assumes that the optical functions n and k, which influence the Kerr rotation, do not change considerably below 200 K. The Co contribution to θ_K at 2.8 eV, $\theta_{K,2.8}^{\mathrm{Co}}(T)$, can be estimated from the Kerr spectra at a temperature T_0 where the S-shaped structure, and hence the ordering of the magnetic moments of the EuS phase, has disappeared. This is the case at $T_0=200$ K. $\theta_{K,2.8}^{\mathrm{Co}}(T)$ then follows at lower temperature from the scaling relation

$$\theta_{K,2.8}^{\mathrm{Co}}(T)\cong\theta_{K,1.1}^{\mathrm{Co}}(T)\,\theta_{K,2.8}^{\mathrm{Co}}(T_0)/\theta_{K,1.1}^{\mathrm{Co}}(T_0). \tag{3}$$

The Kerr rotation at 1.1 eV, $\theta_{K,1.1}^{\mathrm{Co}}(T)$, corresponds predominantly to the Co contribution. This is because EuS does not have electronic transitions below the gap at 1.65 eV and, as a result, the Kerr rotation of EuS is very small at 1.1 eV.[18] Finally, the EuS contribution is the difference between $\theta_K(T)$ at 2.8 eV and $\theta_{K,2.8}^{\mathrm{Co}}(T)$. This procedure can be applied to the peak at 2.15 eV as well yielding the same T_C enhancement to within 10 K. A compensation point T_{comp} is defined by the zero crossing of the EuS contribution between 80 and 90 K while $T_{C,\mathrm{EuS}}$ reaches 160 K. Therefore, the Curie temperature of the EuS phase is enhanced through the antiferromagnetic exchange coupling to the Co matrix by an order of magnitude as compared to T_C of bulk EuS.

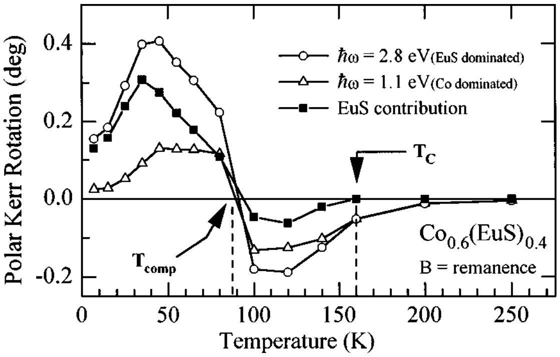

FIG. 4. Extraction of the EuS contribution from the temperature-dependent Kerr spectra of $Co_{0.6}(EuS)_{0.4}$ using the θ_K values at 1.1 and 2.8 eV. Compensation point and Curie temperature are marked by an arrow.

As an independent verification of the large enhancement of $T_{C,\mathrm{EuS}}$, the remanent magnetization has been measured by a SQUID magnetometer in order to measure T_{comp}. The results are shown in Fig. 5 for two sequences: First, at each temperature a magnetic field of 2.7 T is applied prior to measuring the remanent magnetization (■). Second, the field is only applied once at the lowest temperature (△). The compensation point is clearly seen and is close to 90 K in good agreement with the magnetooptically derived value. The slight difference between the two sequences is due to the finite relaxation time of the magnetization after applying a magnetic field. No difference could be found, on the other hand, between field-cooled and zero-field-cooled measurements.

The EuS contribution to the Kerr spectra as a function of temperature and the resulting T_C enhancement have been derived for all EuS concentrations. The result is plotted in

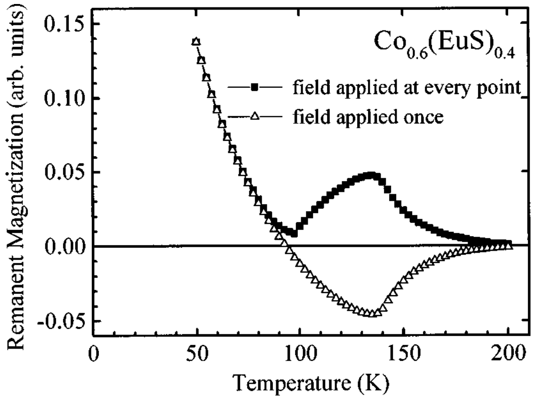

FIG. 5. Remanent magnetization of $Co_{0.6}(EuS)_{0.4}$ as a function of temperature. A field of 2.7 T was applied prior to measuring the first point at 5 K (△) and prior to each temperature (■) in order to align the magnetic domains.

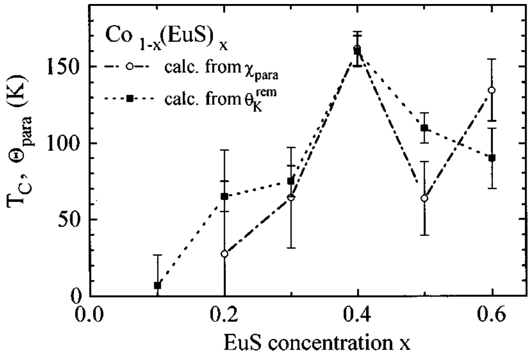

FIG. 6. Curie temperature of the EuS phase as derived from the temperature dependence of the remanence Kerr spectra (■) and from the high-field susceptibility of the Kerr hysteresis loops at room temperature (○).

Fig. 6 in combination with the paramagnetic Curie temperature Θ_{para} as derived from the high-field susceptibility $\kappa\chi_{\text{para}}$ of the Kerr hysteresis loops at room temperature. Note the large correspondence between both curves. The ordering temperature peaks at an EuS composition $x = 0.4$ close to the percolation threshold.

What is the nature of such a strong exchange coupling between macroscopic phases? Evidently, the nanometer size of the EuS precipitate particles is connected with the interesting magnetic properties of the compound. Let us estimate the mean free path, $\lambda_{\text{Co}} = v_F \tau$, of electrons in Co by a free-electron model. Using equations for the Fermi velocity, $v_F = \hbar(3\pi\omega_p^2/4m^{*2}e^2)^{1/3}$, and the relaxation time, $\tau = 4\pi\sigma_0/\omega_p^2$, and assuming for Co a dc conductivity, $\sigma_0 = 1.72\times 10^7\ \Omega^{-1}\ \text{m}^{-1}$ at room temperature and a plasma frequency[19] $\omega_p = 1.17\times 10^{16}\ \text{s}^{-1}$, we get $\lambda_{\text{Co}} = 12$ nm. This is of the same size as the precipitate EuS particles that should hence act as strong scattering sites. The occurrence of a negative magnetoresistance effect of $\delta\rho/\rho = 2\%$ is consistent with this assumption.[13]

Regarding T_C enhancement and antiferromagnetic exchange, it is well known from earlier work on rare-earth chalcogenides[9,18,20] that adding to EuX (X = O, S, Se, Te) a trivalent ion, as, e.g., Gd, Tb, or Y, leads to a T_C enhancement of up to 140 K. However, the magnetic exchange is always ferromagnetic and can be explained in terms of a Ruderman-Kittel-Kasuya-Yoshida-type interaction. The addition of Co, Fe, or Ni can only be done at low concentrations without destroying the NaCl structure. Again, a T_C enhancement up to 190 K is observed in Fe-doped EuO but the exchange is once more ferromagnetic.[8] The effect was theoretically described by the formation of a cluster of EuO spins that are exchange coupled to the impurity transition metal at the center.[21] The exchange is mediated by an f-d interaction and a single impurity ion can couple 2000 spins.

An antiferromagnetic exchange between rare-earth ions and transition metals exists in rare-earth–transition-metal alloys[22] and multilayers.[6,7] The heavy rare-earth elements (e.g., Gd, Tb) exhibit an antiferromagnetic coupling to the magnetic transition metals (Co, Fe), while the light rare-earth elements (e.g., Nd) are ferromagnetically coupled. Alloying with Eu yields[23] divalent Eu^{2+} that is isoelectronic with trivalent Gd^{3+} so it is likely that a Eu^{2+} transition-metal alloy is antiferromagnetically coupled at low temperatures. However, Kerr measurements in $\text{Eu}_x(\text{CoFe})_{1-x}$ give no evidence of an antiferromagnetic coupling at room temperature or a contribution of the Eu^{2+} $4f \rightarrow 5d$ transition to the Kerr effect down to 100 K.[23] Therefore, the fact that Eu is in the EuS crystal field plays an important role in establishing an antiferromagnetic exchange to the Co matrix and in retaining the good magnetooptic properties of EuS.

We have found that in Co(EuS) the T_C enhancement is largest near the percolation threshold. There, the intermixing between the two phases is the largest while still having metallic conductivity in order to guarantee magnetic ordering of the Co phase. Due to the crystalline nature of the EuS phase, the Eu is forced to be divalent. The small size of the precipitate EuS particles leads to a very large surface-to-volume ratio yielding close proximity to the Co phase. Assuming in a spherical EuS crystallite of 10 nm diameter a shell of thickness of one lattice constant a_{EuS} interacting with the Co matrix yields a volume fraction of 32% of an EuS crystallite participating in the exchange. A thickness of $2a_{\text{EuS}}$ even results in 56%. So, in fact, the phase-separated material exactly creates a hypothetical Eu^{2+} transition-metal alloy similar to an amorphous Gd-Co alloy. This would explain the antiferromagnetic exchange coupling between the EuS precipitate particles and the Co matrix.

The large enhancement of T_C, however, is not completely understood at the moment. It seems most likely that a change of the band structure occurs in the EuS particles due to their small size and the close proximity to the Co matrix. The metallic Co matrix could induce a small amount of electrons into the conduction band of EuS. In addition, sulfur vacancies in the EuS crystallites, which are created during deposition,[24] could provide additional negative charge carriers. Both effects would enhance the probability of filling in conduction-band states in EuS. This would immediately increase the exchange interaction, which is thought to be mediated by an indirect interaction between virtually excited conduction electrons and the localized Eu $4f$ states.[25–27] As a consequence, $T_{C,\text{EuS}}$ of the EuS particles will be enhanced. An increase of the direct overlap of the $4f$ states seems unlikely as by finite size effects the bands usually become more localized.

CONCLUSION

In conclusion, we have found an increase in T_C by an order of magnitude in EuS that is induced by a strong antiferromagnetic exchange interaction to a Co matrix. In these macroscopic ferrimagnets, nanocrystalline precipitate EuS particles exist in the high-spin state of divalent Eu^{2+}. They couple, due to the nanometer size, effectively to the metallic Co matrix yielding an antiferromagnetic exchange interaction similar to (Gd, Tb)-Co alloys and multilayers. The large increase in T_C strongly hints at a change in the band structure of the EuS nanocrystallites.

ACKNOWLEDGMENTS

This work has been supported in part by the German Federal Ministry of Education, Science, Research, and Technology (BMBF) under Grant No. FKZ 13N6178/2. We thank D. Menzel for performing the magnetization measurements.

[1] M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).

[2] G. Binasch, P. Grünberg, F. Saurenbach, and W. Zinn, Phys. Rev. B **39**, 4828 (1989).

[3] S. S. P. Parkin, N. More, and K. P. Roche, Phys. Rev. Lett. **64**, 2304 (1990).

[4] A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3745 (1992).

[5] R. J. Gambino and P. Fumagalli, IEEE Trans. Magn. **30**, 4461 (1994).

[6] N. Sato, J. Appl. Phys. **59**, 2514 (1986).

[7] N. Sato and K. Habu, J. Appl. Phys. **61**, 4287 (1987).

[8] K. Y. Ahn, K. N. Tu, and W. Reuter, J. Appl. Phys. **42**, 1769 (1971).

[9] P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earth*, edited by K. A. Gschneider and L. R. Eyring (North-Holland, Amsterdam, 1979), Vol. 2, p. 507.

[10] R. J. Gambino, R. R. Ruf, and N. A. Bojarczuk, J. Appl. Phys. **75**, 6871 (1994).

[11] P. Schwob, Phys. Kondens. Mater. **10**, 186 (1969).

[12] H. Neff, *Grundlagen und Anwendung der Röntgen-Feinstruktur-Analyse* (Oldenburg, München, 1959), p. 292.

[13] R. J. Gambino and J. Wang, Scr. Metall. Mater. **33**, 1877 (1995).

[14] P. Fumagalli, C. Spaeth, U. Rüdiger, and R. J. Gambino, IEEE Trans. Magn. **31**, 3319 (1995).

[15] D. D. Berkner, Phys. Lett. **54A**, 396 (1975).

[16] P. Fumagalli, Ph.D. thesis No. 9082, Swiss Federal Institute of Technology, 1990.

[17] P. Poulopoulos, M. Farle, U. Bovensiepen, and K. Baberschke, Phys. Rev. B **55**, R11 961 (1997).

[18] R. J. Gambino, P. Fumagalli, R. R. Ruf, T. R. McGuire, and N. A. Bojarczuk, IEEE Trans. Magn. **28**, 2973 (1992).

[19] L. Ward, in *Handbook of Optical Constants of Solids*, edited by E. A. Palik (Academic, New York, 1991), Vol. 2, p. 435.

[20] R. J. Gambino, R. R. Ruf, T. R. McGuire, and P. Fumagalli, J. Appl. Phys. **70**, 6386 (1991).

[21] E. L. Nagaev, Fiz. Tverd. Tela (Leningrad) **11**, 3438 (1969) [Sov. Phys. Solid State **11**, 2886 (1970)].

[22] J. M. D. Coey, J. Appl. Phys. **49**, 1646 (1978).

[23] D. Weller and W. Reim, Appl. Phys. A: Solids Surf. **49**, 599 (1989).

[24] R. J. Gambino, R. R. Ruf, and P. Fumagalli, J. Appl. Phys. **73**, 6109 (1993).

[25] S. Methfessel, Z. Angew. Phys. **18**, 414 (1965).

[26] S. Methfessel and D. C. Mattis, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1968), Vol. XVIII/1, p. 389.

[27] T. Kasuya, IBM J. Res. Dev. **14**, 214 (1970).