Temperature dependence of magnetic properties and magnetic interactions in YCo_5/Y_2Co_{17} nanocomposite powders

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Abstract

We have used dc magnetization to measure the temperature dependences of the coercivity, squareness and maximum energy product for YCo_5(70 wt%)/$Y2Co_{17(}$30 wt%) nanocomposite powders synthesized by mechanical milling and subsequent annealing. Our data show that all the above magnetic quantities have values that monotonically increase upon cooling within the 295–3K temperature interval. On the other hand, hysteresis loops collected at low temperatures exhibit a ‘knee’ in the second quadrant of the demagnetization curve, which suggests that the inter-grain exchange coupling becomes less effective as the temperature is lowered. This cooling-induced weakening of exchange coupling, which is somewhat not expected to coexist with the magnetic property enhancement, is confirmed by the temperature dependence of the exchange-coupled volume ratio. Furthermore, the observed temperature behaviour of the coercive field yields evidence that the magnetostatic (dipolar) interactions are strengthened at low temperatures. We explain the low-temperature magnetic property enhancement by anisotropy modifications and the reduction of thermal fluctuations upon cooling, which compete with the weakening of exchange coupling and the enhancement of demagnetizing dipolar interactions.

Introduction

Magnetic nanosystems, such as magnetic nanoparticle ensembles [1, 2] or materials with nanosize grains [3, 4], often exhibit properties that are much different from their bulk counterparts. In particular, materials consisting of a mixture of a hard and a soft magnetic nanophase have attracted much attention due to their potential for permanent magnet development [5]. The functionality of these systems is believed to be based on a strong exchange coupling between the two magnetic phases, which causes the magnetization vectors of the soft and hard components to align and enhances the squareness M_r /M_{max} to values above 0.5 (here M_r is the remanent and M_{max} is the maximum magnetization). Combined with the high coercivity ensured by the presence of the hard magnetic phase, this leads to a maximum energy product $(BH)_{max}$ whose value can be much greater in exchangecoupled magnetic nanocomposites than in isotropic, noncoupled nanomagnets [6–9]. Consequently, many theoretical and experimental investigations have addressed the origin and the effects of exchange coupling on the magnetic properties of nanocomposite materials [5, 10–12]. A first important finding (on which there is widespread agreement) is that the microstructure and grain sizes of the two phases have a strong influence on the exchange coupling. For example, Skomski and Coey [5] have shown that in order to achieve an effective exchange interaction the soft phase grain size should not exceed about twice the domain-wall thickness of the hard phase. In addition, for practical purposes, it was proposed that an optimal exchange coupling is obtained when the average grain size in both phases is in the 10–15 nm range [7]. More recently, a number of studies have also investigated the effect of temperature on the exchange interactions and the

macroscopic properties of composite nanomagnets. Liu *et al* [13] measured hysteresis loops on $PrCo_{3.5}$/Co nanocomposites at different temperatures and observed that the squareness monotonically decreases as new features appear in the demagnetization curve upon lowering the temperature from 300 to 5K. They attributed this behaviour to the so-called (exchange) 'decoupling' that was associated with the thinning of the domain walls in the hard phase. Yin et al [14] reported a similar modification of the demagnetization curve profile upon cooling $Pr_2Fe_{14}B$/α-Fe samples. Yet high remanence and coercivity values observed at low temperatures led these authors to the conclusion that the magnetization curve distortion should not be attributed to decoupling, but to a pronounced difference between the temperature dependences of the anisotropy constants of the hard and soft phases. To gain more insight into the temperature behaviour of exchange coupling in magnetic nanocomposites we carried out a temperature-resolved study of the magnetic properties of YCo_5(70 wt%)/Y_2Co_{17}(30 wt%) powders synthesized by mechanical milling followed by annealing. In a previous work [15] we determined the annealing conditions that maximize the exchange coupling in this nanocomposite at room temperature. Here we report results from dc magnetization measurements carried out on YCo_5/Y_2Co_{17} samples within a broad temperature interval between 3 and 295 K. We found that the squareness M_r /M_{max}, the coercivity HC and the maximum energy product $(BH)_{max}$ increase upon cooling. Concomitantly, a 'knee' develops in the second quadrant of the demagnetization curve, suggesting that the inter-grain exchange coupling becomes less effective as the temperature is lowered. The temperature dependence of the exchange-coupled volume

ratio confirms this coolinginduced weakening of exchange coupling. Moreover, our data demonstrate that the long-range dipolar interactions are enhanced at lowtemperatures. We explain the low-temperature magnetic property enhancement by the increase of anisotropy in the hard phase and the reduction of the thermal fluctuations upon cooling, which have effects that compete with the weakening of exchange coupling and the enhancement of demagnetizing dipolar interactions.

Experimental details

The starting materials were Y and Co ingots with purity of 99.9% and 99.8%, respectively. Alloys with a nominal composition of YCo_5 and Y_2Co_{17} were prepared by arc melting pure elements in an Ar atmosphere. The ingots were turned and re-melted four times to ensure homogeneity. The as-cast ingots were then coarsely pulverized and mixed to obtain about 3 g of YCo_5 (70 wt%)/Y_2Co_17 (30 wt%) powders.

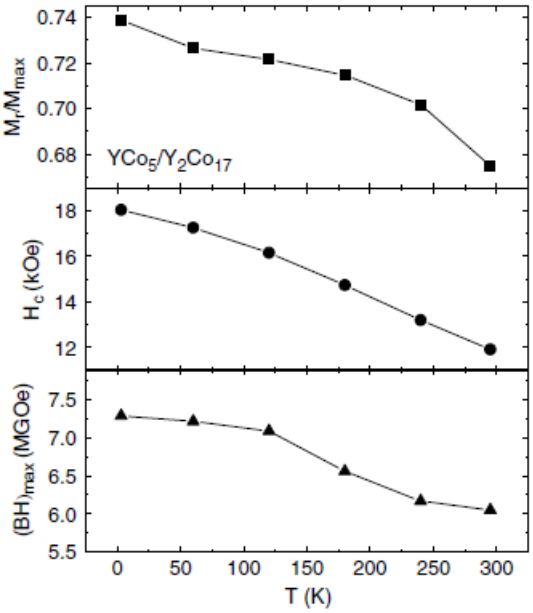

Figure 1. Coercivity, squareness and maximum energy product as a function of temperature for YCo_5(70%)/Y_2Co_{17}(30%) annealed at 1073 K for 1.5 min.

Afterwards, the powders were mechanically milled for 240 min under Ar atmosphere using a SPEX 8000 ball mill with a powder-to-balls ratio of 1 : 8. The as-milled amorphous material was annealed at 1073K for 1.5 min in high vacuum vycor tubes, followed by quenching inwater. X-ray diffraction analysis was performed on finely ground powders using an automated Siemens D5000 diffractometer with a graphite monochromator (Cu Kα radiation). Magnetic hysteresis loops were measured on a Quantum Design Physical Property Measurement System in fields up to 70 kOe at six different temperatures T , ranging from 3 to 295 K. At each T , the squareness M_r /M_{max}, coercivity H_C and maximum energy product (BH)max were determined from the corresponding hysteresis loops.

Results and discussion

The XRD analysis [15] demonstrates that the sample is an impurity-free mixture of YCo_5(70 wt%) andY2Co17 (30 wt%), where the average grain sizes are 12 nm and 14 nm for the hard (YCo_5) and the soft (Y_2Co_{17}) phases, respectively.

Figure 1 shows the temperature dependences of the squareness M_r /M_{max}, coercivity H_C and maximum energy product $(BH)_{max}$ obtained from magnetic hysteresis loops recorded within the 295–3K temperature interval. The data show that all three above-mentioned magnetic quantities monotonically increase upon cooling. For example, HC increases by more than 40% when the temperature is lowered from 295K to 3 K, whereas $(BH)_{max}$ is enhanced by ~15% upon cooling within the same temperature interval. This behaviour seems to indicate that the magnetizing exchange

interactions between the hard phase and the soft phase grains are stronger at low temperatures.

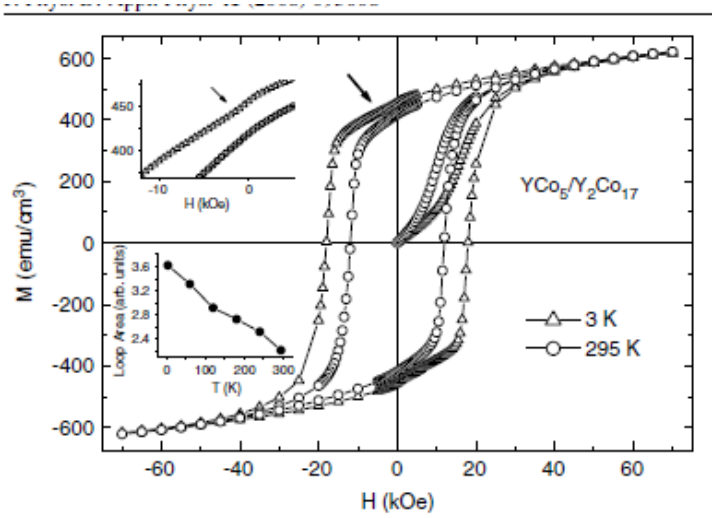

Figure 2. Hysteresis loops from YCo_5(70 wt%)/Y_2Co_{17}(30 wt%) nanocomposite powders measured at 3 and 295 K. The small 'knee' in the 3 K data (indicated by the arrow) suggests that the exchange coupling becomes less effective at low temperatures. The lower inset shows the temperature dependence of the area closed by the $M(H)$ curves.

Interestingly, however, a close inspection of the hysteresis profiles measured at different temperatures suggests a different temperature dependence of the inter-grain magnetic interactions. The M versus H loops recorded at 295K and 3K are shown in figure 2. First, we notice that the shapes of the virgin magnetization curves indicate the same pinning-type magnetization mechanism as the one reported for YCo_5 nanostructured powders [16–18]. In addition, the maximum magnetization M_{max} changes little with $_T$ and has a value that is very close to the one found in monophase YCo_5 [17, 18]. This is most likely due to the similarity between the saturation magnetization in nanostructured YCo_5 and Y_2Co_{17} [19]. Yet, the most important result in figure 2 is the difference between the hysteresis loop profiles measured at 3 and 295 K.

Indeed, the demagnetization curve recorded at 295K has a smooth convex profile that, according to Kneller and Hawig [10], corresponds to a fully exchange-coupled nanocomposite, while, at 3K, the loop profile exhibits a small ‘knee’ in the second quadrant. As mentioned above, this feature has been interpreted by some authors as a signature of exchangecoupling weakening [13], while others have indicated that such ‘decoupling’ cannot occur concomitantly with the magnetic property enhancement upon cooling [14]. Interestingly, and somewhat surprisingly, our data reveal both a distortion of the demagnetization curve at low T (best shown in the upper inset) and an enhancement of the magnetic properties upon cooling, demonstrated by the temperature dependence of the area closed by the M(H) curves (lower inset). To clarify this behaviour, we investigated the effect of temperature on the magnetic interactions in our nanostructured YCo_5/Y_2Co_{17} samples. We first analysed the temperature dependence of the exchange-coupled volume ratio R.

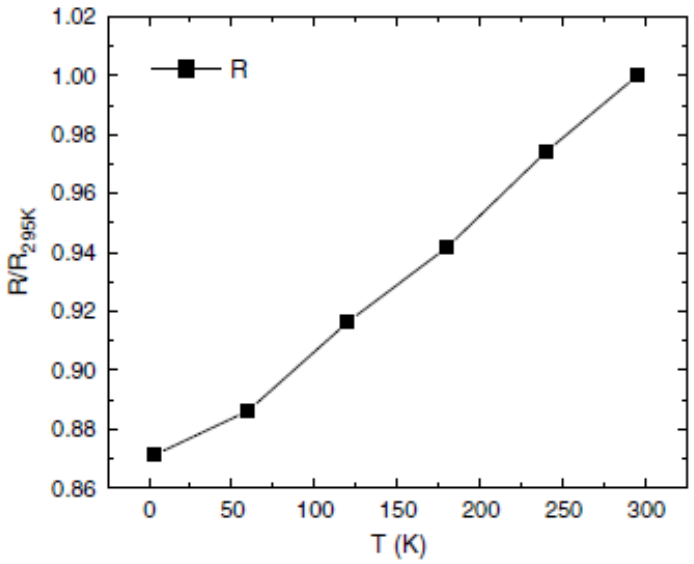

Figure 3. Temperature dependence of the exchange-coupled volume ratio *R* normalized to its room-temperature value.

The exchange-coupled volume ratio was introduced by Dahlgren and Grossinger [20] who noted that whenever the exchange length lex is shorter than the average grain size D in a nanostructured magnet, only a fraction of the total volume is exchange coupled. According to [20], R is defined as

$$R = \frac{V_{\text{coupled}}}{V_{\text{total}}} = 1 - \left(1 - 2 \cdot \frac{l_{\text{ex}}}{D}\right)^3. \qquad (1)$$

Equation (1) holds both for isotropic, single phase nanomagnets and for two-phase (hard/soft) magnetic nanocomposites. For the latter, the exchange length can be written as $l_{ex} = \sqrt{A/K_{eff}}$, where$K_{eff} = f_{soft} \cdot K_{soft} + f_{hard} \cdot K_{hard}$ is an effective anisotropy 'constant' [5]. f_{soft} and f_{hard} are the weight fractions of the two phases, whereas K_{soft} and K_{hard} are the temperature-dependent anisotropy parameters for the soft and hard phases, respectively. In our case, using the temperature dependences of the anisotropy parameters for the hard YCo_5 and the softY_2Co_{17} phases [21], as well as an average grain size D = 13 nm (for the entire sample), we determined the temperature behaviour of the exchange-coupled volume ratio for the YCo_5(70 wt%)/Y_2Co_{17}(30 wt%) nanocomposite. This is shown in figure 3 where R, normalized to its room-temperature value, is plotted versus T within the interval between 295 and 3K.We observe that R monotonically decreases as the temperature is lowered, indicating that the exchange-coupled volume at 3K is smaller (by about 10%) than its room-temperature counterpart. Obviously, this is a direct result of the temperature variation of the anisotropy parameters in YCo5 (K_{hard}) and Y_2Co_{17} (K_{soft}). The *R* versus *T* behaviour is in good agreement with the distortion of the magnetic hysteresis loop observed at low

temperatures (figure 2), suggesting that the 'knee' in the second quadrant of the 3Kdemagnetization curve is, indeed, due to a less complete *exchange coupling* induced by cooling. The small magnitude of the distortion (compared with the ones observed in [13, 14]) is also in good agreement with the 10% reduction of *R* upon cooling from 295 to 3K.

To get more insight into the low-temperature behavior of the inter-grain magnetostatic (dipolar) interactions in YCo_5/Y_2Co_{17} we followed the temperature behaviour of its coercive field H_C. In the theory of micromagnetism H_C can be described by an extended version of Brown's equation [22]:

$$H_C = \alpha_K \cdot H_N - N_{eff} \cdot M_S, \qquad (2)$$

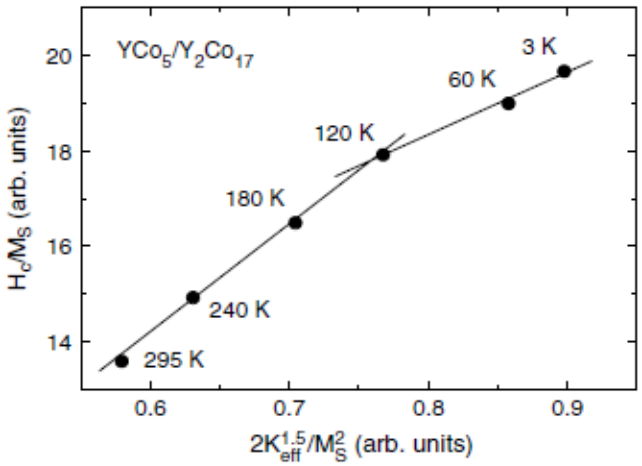

Figure 4. H_C/M_S versus $2K_{eff}^{1.5}/M_S^2$ for temperatures between 3 and 295 K. The two solid lines are linear fits to the data within the 3–120 K and the 120–295 K temperature intervals.

where *αK* and *N*eff are microstructural parameters that account for the non-ideal reversal mechanism, *M*S is the saturation magnetization and *H*N is the nucleation field. For hard magnetic materials with vanishing high order anisotropy constants (such as

YCo_5 [23]) $H_N = 2 \cdot K^{1.5}/M_S$. In our case, pinning is the dominant coercivity mechanism (as indicated by the virgin magnetization curves in figure 2) and, since we deal with a magnetic nanocomposite, $K = K_{eff} = f_{soft} \cdot K_{soft} + f_{hard} \cdot K_{hard}$. Consequently, equation (2) becomes

$$H_C = \alpha_K \cdot \frac{2K_{eff}^{1.5}}{M_S} - N_{eff} \cdot M_S \qquad (3)$$

with $MS = f_{soft} \cdot M_{soft} + f_{hard} \cdot M_{hard}$ the weighed saturation magnetization (M_{soft} and M_{hard} are the saturation magnetizations for the Y_2Co_{17} and YCo_5 phases, respectively [19]). Thus, as the temperature is varied, one should expect a linear dependence of H_C/M_S on $2K\frac{1.5}{eff}/M2\frac{e}{S}$, which would allow the microscopic parameters αK and N_{eff} to be determined. While αK essentially depends on the grain sizes and average microstructure (and therefore should change little with T), N_{eff} is influenced to a great extent by the strength of the dipolar interactions—more precisely, the stronger the dipolar interactions, the greater the absolute value of N_{eff}.

Figure 4 shows the H_C/M_S on $2K\frac{1.5}{eff}/M\frac{2}{S}$ dependence measured upon the variation of T within the 295–3K range. The most notable feature of the data is the presence of two distinct temperature domains over which the linear dependence predicted by equation (3) is confirmed: one between 295 and 120K and another below 120 K. The solid lines represent the best fits of equation (3) to the data collected within the two above-mentioned temperature domains, where α_K and N_{eff} were used as variable parameters. The best fits yield $\alpha_K = 2.2 \times 10^{-5}$ (erg $cm^{-3})^{-1/2}$ and $N_{eff} = -0.4$, for

120K < T < 295 K, and α_K = 1.3 × 10−5 (erg cm^{-3}) $^{-1/2}$ and N_{eff} = −7.7, for 3K < T < 120 K. Expectedly, α_K exhibits a small value, which is consistent with the nanometric size of the grains. Also, αK changes little upon cooling, as the grain sizes and average microstructure are not substantially affected by T . On the other hand, the absolute value of N_{eff} in the 3–120K temperature interval is almost *20 times greater* than its T > 120K counterpart, indicating that the long range demagnetizing dipolar interactions are enhanced at low temperatures. Significantly, this is consistent with the $(BH)_{max}$ versus T dependence (shown in figure 1), where an obvious change in the slope occurs at about 120 K. Indeed, upon cooling from 120 to 3K, $(BH)_{max}$ increases only slightly although the coercivity increases by more than 12%. This clearly hints at modifications in the magnetic interactions strength below 120 K.

Thus, our data and analysis show that not only does the exchange coupling weaken but the dipolar interactions become stronger upon cooling a YCo_5(70 wt%)/Y_2Co_{17}(30 wt%) nanostructured sample from room temperature to 3K. Interestingly, this happens concomitantly with the enhancement of the coercivity H_C, squareness M_r /M_{max} and the maximum energy product (BH)max of the title spring magnet. Such enchancement has usually been associated with a strong exchange coupling. Yet, in our case, several factors contribute to the abovementioned temperature behaviour of the magnetic properties. First, the weakening of the thermal fluctuations upon cooling compensates for the reduction of the exchange-coupled volume and the strengthening of the dipolar interactions, ensuring that M_r /M_{max} does not decrease upon cooling (which would be the expected effect of exchange ‘decoupling’)

but actually exhibits a modest (8%) increase when T is lowered from 295 to 3K. Second, the sizeable increase of the anisotropy in the hard phase K_{hard} upon cooling has a dual effect. On the one hand it contributes to the overall anisotropy (K_{eff}) increase, which, in turn, leads to the reduction of the exchange-coupled volume at low temperatures (according to equation (1)). On the other hand, the enhancement of K_{hard} is the main factor responsible for the 40% increase of the coercive field H_C upon cooling from 295 to 3K. While the effect of the hard phase anisotropy increase on H_C is not unexpected [24], it has been indicated [13] that such an increase might *also* drastically reduce the effectiveness of the inter-grain exchange coupling leading to a poor maximum energy product. Obviously, this is *not* the case for our YCo_5/Y_2Co_{17} nanocomposite. Here, the low-temperature weakening of exchange coupling—although evident in both our data (low-*T* 'knee') and our*R* versus *T* calculations (10% reduction in *R* upon cooling)—does not have enough 'magnitude' to overcome the competing effect of the reduction in thermal fluctuations. Consequently, M_r/M_{max} is actually slightly larger at 3K than its room-temperature counterpart. This temperature behaviour of the squareness together with the above-mentioned cooling-induced coercivity enhancement explains the ~15% increase in the maximum energy product observed upon the lowering of *T* from 295 to 3K.

Summary

We have synthesized YCo_5(70 wt%)/Y_2Co_{17}(30 wt%) nanocrystalline powders by mechanical milling followed by annealing and used dc magnetization to measure their coercivity H_C, squareness M_r/M_{max} and the maximum energy product $(BH)_{max}$.

monotonically increase when the temperature *T* is lowered from 295 to 3 K. Our data also show that the lowering of *T* results in a less effective exchange coupling between adjacent grains and stronger demagnetizing dipolar interactions. We attribute the magnetic property enhancement upon cooling to the reduction of the thermal fluctuations and the increase of the anisotropy in the hard phase, as both these phenomena have effects that compete with the weakening of the exchange coupling and the strengthening of the dipolar interactions.

References

[1] Zhang L, Luo J and Chen Q 2005 J. Phys.: Condens. Matter 17 5095

[2] Elizalde Galindo J T, Adair A H, Botez C E , Corral Flores V, Bueno Baques D, Fuentes Cobas L and Matutes-Aquino J A 2007 Appl. Phys. A 87 743

[3] Jin Z Q, Thadhani N N, McGill M, Li J, Ding Y, Wang Z L, Zeng H, Chen M, Cheng S F and Liu J P 2004 J. Appl. Phys. 96 3452

[4] Trukhanov S A, Trukhanov A V, Botez C E, Adair A H, Szymczak H and Szymczak R 2007 J. Phys.: Condens. Matter. 19 266214

[5] Skomski R and Coey J M D 1993 Phys. Rev. B 48 15812

[6] Al-Omari I A and Sellmyer D J 1995 Phys. Rev. B 52 3441

[7] Manaf A, Buckley R A and Davies H A 1993 J. Magn. Magn.

Mater. 128 302

[8] Fischer R, Schrefl T, Krom¨uller H and Fidler J 1996 J. Magn. Magn. Mater. 153 35

[9] McCormick G, Miao W F, Smith P A I, Ding J and Street R 1998 *J. Appl. Phys.* **83** 6256

[10] Kneller E F and Hawig R 1991 *IEEE Trans. Magn.* **27** 3588

[11] Cui B Z, Sun X K, Liu W, Zhang Z D, Geng D Y and Zhao X G 2000 *J. Appl. Phys.* **87** 5335

[12] Zhang M, Ren W J, Zhang Z D, Sun X K, Liu W, Geng D Y, Zhao X G, Gr¨ossinger R and Triyono D 2003 *J. Appl. Phys.* **94** 2602

[13] Liu J P, Skomski R, Liu Y and Sellmyer D J 2000 *J. Appl. Phys.* **87** 6740

[14] Yin J H, Sun Z G, Zhang Z R, Zhang H W and Shen B G 2001 *J. Appl. Phys.* **89** 8351

[15] Elizalde Galindo J T, Botez C E, Rivera G´omez F and Matutes-Aquino J A 2007 *Phys. Lett.* A **336** 110

[16] Bertotti G 1998 *Hysteresis in Magnetism for Physicists, Materials Scientists and Engineers* (San Diego, CA: Academic)

[17] Tang N, Chen Z, Zhang Y, Hadjipanayis G C and Yang F 2000

J. Magn. Magn. Mater. **219** 173

[18] S´anchez J L, Elizalde Galindo J T and Matutes-Aquino J A 2003 *Solid State Commun.* **127** 527

[19] Hoffer G and Strnat K 1967 *J. Appl. Phys.* **38** 1377

[20] Dahlgren M and Gr¨ossinger R 1999 *Mater. Sci. Forum* **302–303** 263

[21] Foner S and McNiff E J Jr 1967 *J. Appl. Phys.* **38** 1377

[22] Crew D C, Girt E, Suess D, Schrefl T, Krishnan K M, Thomas G and Guilot M 2002 *Phys. Rev.* B **66** 184418

[23] Asti G, Bolzoni F, Melville D and Rinaldi S 1975 *IEEE Trans. Magn.* **11** 1437

[24] Hadjipanayis G C 1999 *J. Magn. Magn. Mater.* **200** 373