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2003 J. Phys.: Condens. Matter 15 4623

(http://iopscience.iop.org/0953-8984/15/26/312)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 4623–4630 PII: S0953-8984(03)59002-6

The magnetic properties and reversal of Fe–Co nanowire arrays

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Received 31 January 2003, in final form 29 May 2003
Published 20 June 2003
Online at stacks.iop.org/JPhysCM/15/4623

Abstract

20 nm diameter Fe–Co nanowire arrays with different composition were fabricated by electrodeposition. A nanoporous anodized aluminium oxide film was used as the substrate. The microstructure and magnetic properties were studied by x-ray fluorescence, transmission electron microscopy, x-ray diffraction and vibrating sample magnetometry. Both the coercivity H_c and the spontaneous magnetization M_s increase when the Co content in Fe–Co alloy increases from 0 to about 30 at.%, and then decrease with further increase in the Co content. A model called the 'chain of crystals' is developed and solved to explain the experimental results.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There has been increasing interest in the fabrication and study of nanostructural magnetic materials because of their unusual properties compared with bulk materials. They may also have applications in magnetic recording media, sensors and other devices [1–3]. Many techniques have been developed to produce nanoscale materials. Among them, electrodeposition of nanowires into self-assembled alumites is a simple low-cost, high-throughput technique [4, 5]. We fabricated Fe–Co alloy nanowire arrays employing this method and studied their magnetic properties and reversal.

Magnetic reversal determines the behaviour of the hysteresis loops of the nanowires and has been studied widely before [6–10]. The simplest approach is to model the nanowires as thin and homogeneous prolate ellipsoids of revolution. Yet the simple reversal modes obtained from the above model, such as coherent rotation and curling, cannot account for the observed hysteretic behaviours. For example, it has been well known for decades that the coherent rotation mode greatly overestimates the coercivity of the wire arrays. Wegrowe *et al* [11]

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0953-8984/03/264623+08$30.00

found that their magnetization data could be fitted to the curling prediction only with the paradoxical assumption that the shape of the 'infinite cylinder' was like a rugby ball, with an aspect ratio of the order of 2:1. Our experimental results in this paper also present obvious disagreement with the curling mode.

Recently, Sellmyer *et al* [10, 12, 13] proposed that the failure of the above model may be attributed to the neglect of the imperfections in the structure of nanowires. Since imperfections are inevitable in the fabrication and may have a great effect on the magnetic properties of the nanowires, the previous model for a perfect nanowire should be modified. In [12], a magnetization reversal model based on the coherent rotation mode was developed and solved with two mechanisms taken into account, the soft region and misaligned grains. Yet the results they obtained were very qualitative and only applicable to nanowires with diameters less than the coherent length $l_{coh} = \sqrt{A}/M_s$. To explain the observed magnetic properties of alloy nanowires we fabricated another model taking into account the polycrystallinity of the nanowires, and used this model to explain our experimental data.

2. Experimental details

An annealed Al (99.5%) sheet was anodized in 0.4 M H_2SO_4 for 3 h to get an AAO template. Then it was immersed in 0.3 M H_3PO_4 for 5 min to widen the diameter of the pores. The average diameter of the pores is about 20 nm after this treatment and the centre-to-centre distance between the pores is about 60 nm. Then the Fe–Co alloy was deposited into the pores by ac electrolysis in an electrolyte consisting of $FeSO_4$, $CoSO_4$, boric acid (0.6 M) and ascorbic acid (1 g l^{-1}) at a pH value of about 4.0. The total concentration of $FeSO_4$ and $CoSO_4$ is 0.22 M. The electrolysis was conducted at 15 °C, 50 Hz and 14 V ac for 8–10 min using graphite as the counter-electrode. X-ray fluorescence (XRF) and x-ray diffraction (XRD) were used to investigate the content percentage and crystalline structure of the nanowires. To avoid the interference of Al, specimens were immersed in $CuCl_2$ solution to remove the remaining Al from the substrate before the XRF and XRD investigations were carried out. Transmission electron microscopy (TEM) was used to determine the diameters and lengths of the nanowires (figure 1). The length of the nanowires is about 0.5–1 μm and the diameter is about 20 nm. The magnetic properties were studied by vibrating sample magnetometer (VSM) investigation.

3. Results and discussion

Figure 1 shows some typical TEM images and selected-area diffraction patterns of $Fe_{69}Co_{31}$ and Co. The diffraction ring indicates that the nanowires are polycrystalline. Figure 2 shows the XRD patterns of Fe and $Co_{31}Fe_{69}$. The XRD investigation revealed that they have body-centred cubic structure and preferred ⟨110⟩ orientations along the axis of the wires. The peaks of the Fe nanowires and $Fe_{69}Co_{31}$ nanowires are very near, which indicates that their crystalline structures are very similar.

The magnetic properties of the alloy nanowire arrays were investigated using a VSM. The hysteresis loops of $Co_{34}Fe_{66}$ alloy nanowire arrays are shown in figure 3. It is obvious that the easy axis is perpendicular to the substrate, i.e. parallel to the nanowire due to the shape anisotropy. The coercivities H_c and remanence M_r/M_s, which were measured with the applied field perpendicular to the substrate, are stated in table 1 for the series of Fe–Co nanowire arrays. The magnitude of M_r/M_s is about 0.9. The coercivity increases with increasing Co content from 0 to about 30 at.%, and then decreases with continued increase of the Co content. The Slater–Pauling curve predicts that the spontaneous magnetization M_s of Fe–Co alloy increases

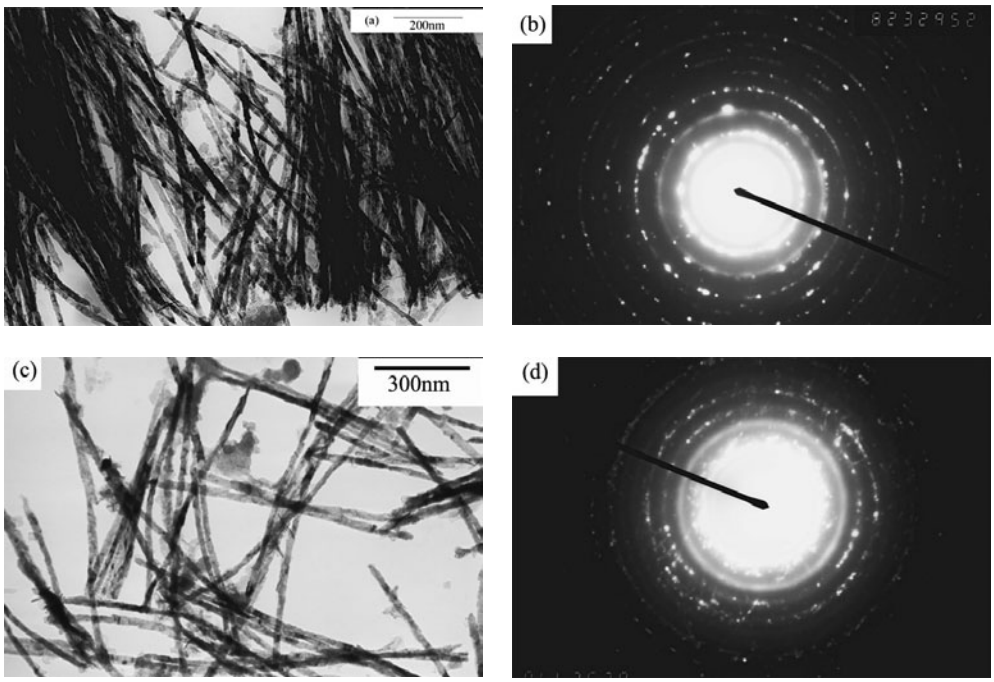

Figure 1. (a) TEM photo of $Fe_{69}Co_{31}$ nanowires. (b) Diffraction ring of $Fe_{69}Co_{31}$. (c) TEM photo of Co nanowires. (d) Diffraction ring of Co.

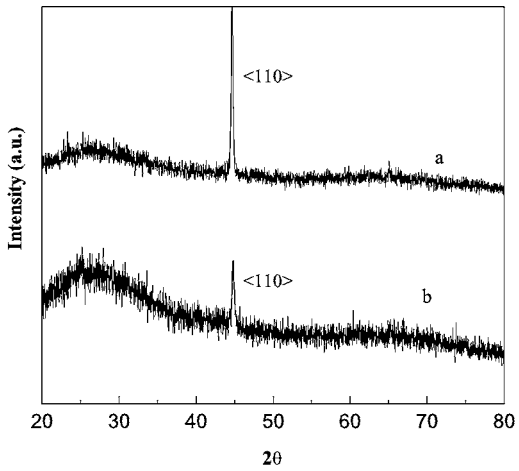

Figure 2. XRD patterns of (a) Fe and (b) $Co_{31}Fe_{69}$.

with Co content and then decreases with Co content above 30 at.% in bulk states [14, 15]. In our experiment, the wires are nanoscaled and the imperfections may decrease M_s as well as the shape anisotropy of the nanowires compared with bulk state materials as presented by Wirth *et al* [17] and Sellmyer *et al* [12]. But for the nanowires fabricated under the same conditions and having the same diameter, the influence of imperfections can be expected to be the same. Following this, we can conclude that the coercivity H_c of the nanowire increases with the increase of its spontaneous magnetization M_s.

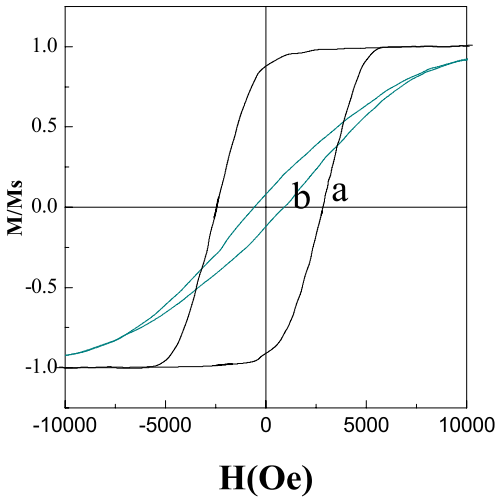

Figure 3. Hysteresis loops of $Co_{34}Fe_{66}$ (a) perpendicular and (b) parallel to the substrate.

Table 1. Perpendicular (to the substrates) coercivities (H_c) and remanence ratios M_r/M_s of the Fe–Co alloy nanowires with different proportions of Fe and Co.

	Fe	$Co_{17}Fe_{83}$	$Co_{28}Fe_{72}$	$Co_{31}Fe_{69}$	$Co_{34}Fe_{66}$	$Co_{38}Fe_{62}$	$Co_{60}Fe_{40}$	Co
H_c (Oe)	2380	2412	2593	2856	2698	2444	2095	1968
M_r/M_s	0.90	0.89	0.88	0.91	0.91	0.90	0.93	0.91

To explain the above experimental results, the magnetization reversal was studied. Previous studies have usually treated the nanowires as perfect infinitely long cylinders or prolate ellipsoids, and two modes of magnetic reversal, coherent rotation and curling, were considered important. When the radius of the wires is less than $l_{coh} = \sqrt{A}/M_s$, which is about 6–9 nm for iron (the exact value is difficult to obtain due to the discrepancy of the exchange constant A of iron given by different workers) and 11 nm for Co, the reversal mode is coherent rotation [9], i.e. the dipole moment rotates uniformly during magnetic reversal. The coercivity obtained is $2\pi M_s$, which equals the shape anisotropic field. This result is about three times higher than the usually observed results, as well as ours. When the radius of the wire is larger than l_{coh}, the magnetic mode is curling. In this case, the coercivity is [8, 9]

$$H_c = 2.16\pi \frac{A}{M_s R^2}, \tag{1}$$

where A is the exchange constant, M_s is the spontaneous magnetization and R is the radius of the wire. We can see that the coercivity from (1) is inversely proportional to M_s, which is contrary to our experimental results. Besides, the value obtained from (1) for 20 nm diameter Fe nanowires is about 4000 Oe and for Co about 12 600 Oe. Both are much higher than the experimental results. Here and the following we neglect the influence of the magnetocrystalline anisotropy for two reasons. One is that the magnetocrystalline anisotropic energy is usually much smaller than the shape anisotropic energy. The other is that for Fe and most Fe–Co alloy nanowires in our experiment, the angle between the magnetocrystalline anisotropy and the nanowire axis is 45°. From the conclusions of Wegrowe *et al* [11], the magnetocrystalline anisotropy is of little importance to H_c in this case.

From the above we can see that the ideal delocalized modes obtained from the perfect cylinder model do not agree with the experimental results. Sellmyer *et al* attribute this failure

to the neglect of the imperfections in the structure of real nanowires. When the imperfections are considered, the magnetic reversal becomes localized, which will lead to a reduction of coercivity. Sellmyer *et al* [12, 13] calculated this reduction caused by local soft regions and grain misalignment, treating the imperfections as perturbations of the coherent rotation mode. Yet since the experimental coercivity is often only one-third of the result from the coherent rotation mode, it is not appropriate to treat the imperfections perturbatively.

In this work we consider that the imperfections, such as the absence of atoms and dislocation, are commonplace at the boundary of two crystals in the nanowire and that these imperfections lead to the absence or weakening of local exchange interaction since the exchange interaction is very short ranged. Then the nanowire can be treated as a chain of single crystals without exchange interaction between adjacent crystals. The simplest case of this model has been studied by Jacob and Bean [6]. According to them, the chain is made up of spheres of the same diameter. Each sphere is considered single domained and has no exchange interaction between adjacent spheres. A reasonable magnetic reversal mode of this model is symmetric fanning, as in figure 4, i.e. the magnitude of the angle of fanning is constant along the axis of the chain. Because the magnetostatic self-interaction energy of each sphere is unchanged during magnetic reversal, the total free energy of the system can be written as

$$E_n = (\mu^2/a^3)nL_n(\cos 2\theta - 3\cos^2\theta) + (\mu^2/a^3)nM_n(1 - 3\cos^2\theta) + n\mu H\cos\theta,$$

where

$$L_n = \sum_{j=1}^{(n-1)/2<j\leqslant(n+1)/2} [n - (2j-1)]/n(2j-1)^3,$$

$$M_n = \sum_{j=1}^{(n-2)/2<j\leqslant n/2} (n - 2j)/n(2j)^3,$$

a is the diameter of the sphere, n is the number of the spheres and also the aspect ratio of the nanowire and $\mu = \pi a^3 M_s/6$ is the dipole moment of a single sphere. In the standard way, the coercivity is obtained as

$$H_{c,n} = \pi(6M_n + 2L_n)M_s/6. \tag{2}$$

Here $H_{c,n}$ is proportional to the spontaneous magnetization M_s, which agrees with our experimental results. The term $6M_n + 2L_n$ is denoted as $C(n)$ which only depends on n. The $C(n)$–n curve is shown in figure 5. $C(n)$ increases quickly for small n, while for $n > 20$ the value $C(n)$ increases slightly with increasing n, consistent with the observation in H_c. These results agree well with those reported by Zeng *et al* [16]. When $n = 25$, $C(n) = 2.81$. Using the $M_s = 1700$ Oe of iron in bulk states, one finds from equation (2) that H_c is about 2500 Oe. For $Co_{31}Fe_{69}$, M_s is about 1930 Oe [14], and H_c from equation (2) is about 2840 Oe. Both are very close to our experimental results in table 1. Figure 6 shows a comparison of experimental coercivity and coercivity calculated using (2).

If we consider the fact that the single crystals in real nanowires are usually prolate, the model of Jacob and Bean should be modified. In this case, the magnetostatic self-interaction energy of each particle is changed during magnetic reversal. If we assume that the chain is made up of prolate ellipsoids of the same size, the total energy can be written as

$$E_m = (\mu^2/b^3)mL_m(\cos 2\theta - 3\cos^2\theta) + (\mu^2/b^3)mM_m(1 - 3\cos^2\theta) + 2\pi m(N_\perp - N_\parallel)M_s\sin^2\theta + m\mu H\cos\theta.$$

Here b is the distance between the centres of two ellipsoids and also the length of the long axis of the ellipsoid, m is the number of ellipsoids and $N_\perp$ and $N_\parallel$ are the demagnetization factors

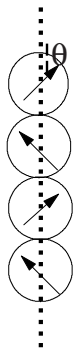

Figure 4. Magnetic reversal mode of a chain of spheres: symmetric fanning.

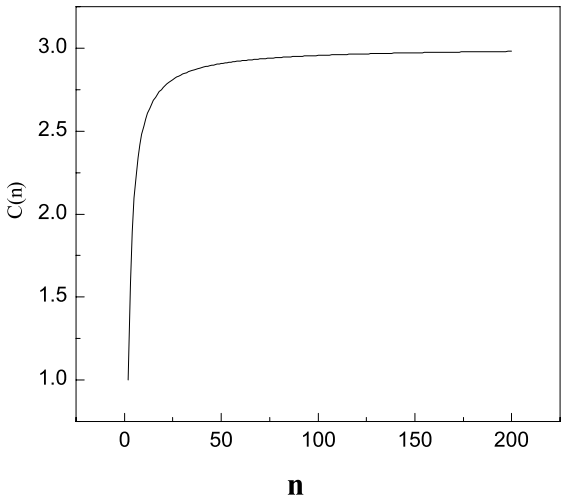

Figure 5. $C(n)$–n curve obtained from the 'chain of spheres' model, where n is the aspect ratio of the nanowires and $C(n)$ is proportional to the coercivity. The $C(n)$–n curve indicates the dependence of the coercivity on the aspect ratio n of the nanowires.

of the ellipsoid perpendicular and parallel to the axis of the nanowires which only depend on the aspect ratio α of the ellipsoid. The coercivity can be obtained as

$$H_{c,m} = (\mu/b^3)(6M_m + 2L_m) + 4\pi(N_\perp - N_\parallel)M_s. \tag{3}$$

Noting that $\mu = \pi a^2 b M_s/6$, we can rewrite $H_{c,m}$ as

$$\begin{aligned} H_{c,m} &= \frac{1}{\alpha^2}\pi(6M_m + 2L_m)M_s/6 + 4\pi(N_\perp - N_\parallel)M_s \\ &= \frac{1}{\alpha^2}\pi C\left(\frac{n}{\alpha}\right)M_s/6 + 4\pi(N_\perp - N_\parallel)M_s, \end{aligned} \tag{4}$$

where $\alpha = b/a$ is the aspect ratio of the ellipsoid and n is the aspect ratio of the nanowire. From (4), we can see that not only the aspect ratio n of the nanowire affects the coercivity, the size of the single crystals making up the nanowire also affects the coercivity. When α increases, the first term of (4) decreases and the second term increases with the total value of $H_{c,m}$ increasing, i.e. the nanowires made up of bigger crystals along the axis have a higher

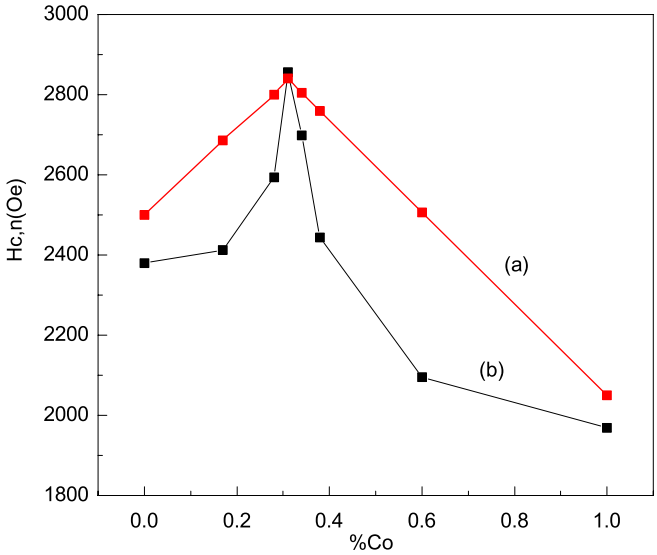

Figure 6. The dependence of the coercivity on the Co content percentage: (a) the results obtained from the 'chain of spheres' model and (b) the experimental results.

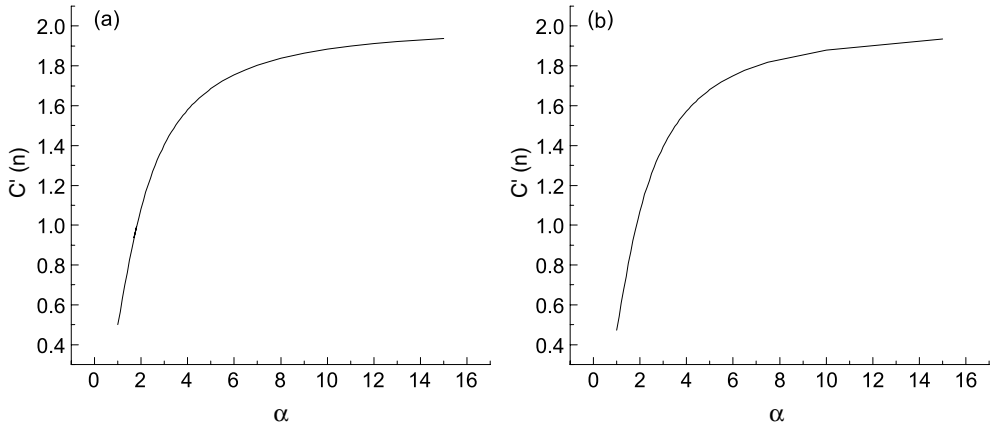

Figure 7. $C'(n)$–α curve obtained from the 'chain of crystals' model, (a) $n = 30$ (b) $n = \infty$, where n is the aspect ratio of the nanowires, α is the aspect ratio of the ellipsoids and $C'(n)$ is proportional to the coercivity. The $C'(n)$–α curve indicates the dependence of the coercivity on the single crystal size.

coercivity. This is confirmed by the experimental result that the coercivity of the nanowire arrays increases remarkably after annealing because the crystals grow bigger along the wire axis after the treatment [13]. We denote $\frac{1}{\alpha^2}C(\frac{n}{\alpha})/6 + 4(N_\perp - N_\parallel)M_s$ as C' which depends on both n and α. The relation of C' and α with $n = 30$ and ∞ is as figure 7. If $\alpha = 1$, i.e. the nanowire is a chain of spheres, $N_\perp = N_\parallel = 1/3$, the result from (4) is as the same with (2). If the nanowire is made up of an infinitely long single crystal, the first term of (4) equals zero, and we get the same results with the coherent rotation mode.

It should also be noted that the above model requires the single crystals to be single domained. For a prolate ellipsoid, the critical radius for single-domain behaviour is $R_c =$

$S_c\sqrt{A}/M_s$, where S_c is a constant varying from 1.04 for a cylinder to 1.44 for a sphere [9]. For an iron sphere, R_c is about 9–12 nm. The exact value is difficult to obtain for the same reason as with the calculation of l_{coh}. If the size of the single crystal is larger than the critical size, the magnetic reversal will become much more complicated as will the calculation of the coercivity.

Finally we make a comparison between the model and the real microstructure of nanowires. Usually, the boundaries of single crystals in real nanowires will greatly weaken the exchange interaction or cause it to vanish between adjacent grains because of imperfections such as absence of atoms or dislocation. So the particle size in the model can be considered approximately equal to the average size of the single crystals of real nanowires. Yet there may also exist some boundaries where the exchange interaction is not weak enough to be neglected. Thus there will exist a discrepancy between the particle size of the model and the crystal size of real nanowires and the model should also be modified. More exact and detailed work about this is needed in future as well as experiments to test the calculations.

4. Summary

In summary, we fabricated Fe–Co alloy nanowire arrays by electrodeposition, studied their magnetic properties and found that their coercivity increases with increase in the spontaneous magnetization of the nanowires. A model called the 'chain of crystals' was developed and used to explain the experimental results. The model also provides explanations for some results observed by other groups.

Acknowledgments

This work was supported by project no 50171033 of the National Nature Science Foundation of China and by the National Key Project of Fundamental Research of China No G1999064508. We are also grateful to Professor Zhai for the helpful discussion and to our colleagues T Lee and Y X Wang for their help in the experiment.

References

[1] Liu K, Nagodawithana K, Searson P C and Chien C L 1995 *Phys. Rev.* B **51** 7381
[2] Sellmyer D J, Yu M, Thomas R A, Liu Y and Kirby R D 1998 *Phys. Low-Dimens. Semicond. Struct.* **1/2** 155
[3] Zheng M, Menon L, Zeng H, Liu Y, Bandyopadhyay S, Kirby R D and Sellmyer D J 2000 *Phys. Rev.* B **62** 12282
[4] Almawlawi D, Coombs N and Moskovits M 1991 *J. Appl. Phys.* **70** 4421
[5] Metzger R M, Konaovalov V V, Sun M, Xu T, Zangari G, Xu B, Benakli M and Doyle W D 2000 *IEEE Trans. Magn.* **36** 30
[6] Jacob I S and Bean C P 1955 *Phys. Rev.* **100** 1060
[7] Brown W F 1957 *Phys. Rev.* **105** 1479
[8] Aharoni A and Shtrikman S 1958 *Phys. Rev.* **109** 1522
[9] Frei E H, Shtrikman S and Treves D 1957 *Phys. Rev.* **106** 446
[10] Skomski R, Zeng H, Zheng M and Sellmyer D J 2000 *Phys. Rev.* B **62** 3900
[11] Wegrowe J-E, Kelly D, Franck A, Gilbert S E and Ansermet J 1999 *Phys. Rev. Lett.* **82** 3681
[12] Zeng H, Skomski R, Menon L, Liu Y, Bandyopadhyay S and Sellmyer D J 2002 *Phys. Rev.* B **65** 134426
[13] Sellmyer D J, Zheng M and Skomski R 2001 *J. Phys.: Condens. Matter* **13** R433
[14] Slater J C 1937 *J. Appl. Phys.* **8** 385
[15] Pauling L 1938 *Phys. Rev.* **54** 899
[16] Zeng H, Zheng M, Skomski R and Sellmyer D J 2000 *J. Appl. Phys.* **87** 4718
[17] Wirth S and Von Molnar S 1999 *J. Appl. Phys.* **85** 5249