



Deposition of epitaxial α -Fe₂O₃ layers for exchange bias studies by reactive dc magnetron sputtering

C. LEIGHTON^{†||}, A. HOFFMANN[‡], M. R. FITZSIMMONS[‡], J. NOGUÉS[§] and
IVAN K. SCHULLER[†]

[†] Physics Department, University of California, San Diego, La Jolla, California
92093-0319, USA

[‡] Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

[§] Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra,
Spain

[Received 20 February 2001 and accepted 25 April 2001]

ABSTRACT

We describe the deposition and characterization of epitaxial thin films of the iron oxide haematite (α -Fe₂O₃), a promising candidate for fundamental studies of exchange anisotropy as well as for high thermal stability applications. The films were deposited by reactive dc magnetron sputtering. Structural characterization was by large-angle X-ray diffraction and grazing-incidence reflectivity (with the scattering vector normal to the sample plane), in-plane grazing-incidence diffraction (scattering vector in the sample plane) and reflection high-energy electron diffraction. Optimized sputtering conditions result in good epitaxy both in the growth direction and in the plane, as well as very smooth surfaces.

§1. INTRODUCTION

Exchange anisotropy is a long-standing problem in condensed-matter physics which remains essentially unsolved (Meiklejohn and Beam 1956, Berkowitz and Takano 1999, Nogués and Schuller 1999). The emergence of field-sensing devices which use exchange biasing to pin ferromagnetic layers (Dieny *et al.* 1991) has led to a renewed interest in the fundamental mechanisms of exchange biasing. Many material systems, useful from the application point of view or suitable for fundamental studies, have been investigated. In this paper we report the successful deposition of epitaxial iron oxide α -Fe₂O₃ (haematite), which is interesting in terms of fundamental studies of exchange anisotropy as well as being a possible candidate for a high-thermal-stability insulating pinning layer for ferromagnetic layers in hybrid spin valves.

Haematite is an insulating oxide with a rhombohedral crystal structure whose magnetic phase diagram is well understood (Creer *et al.* 1980, Morrish 1994). A transition from paramagnetism to antiferromagnetic ordering occurs at a very high Néel temperature T_N of approximately 700°C (Morrish 1994, p. 52). Below this temperature an unusual canted ground state is evident down to the Morin

^{||} Present address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis 55455, USA. Email: leighton@cems.umn.edu

transition temperature T_M of approximately 260 K (Morin 1950, Morrish 1994, p. 53). This canted antiferromagnetism leads to a net imbalance of the projected moment on each sublattice and hence a finite moment, or 'weak' ferromagnetism (Morrish 1994, p. 55). At T_M the spins reorient from the hexagonal planes to lie along the c axis, resulting in simple antiferromagnetic ordering. This system provides a simple and well-understood spin structure, where the spin orientation changes from the interfacial plane to its normal on reducing temperature.

From the applied point of view the high T_N is attractive as a possible antiferromagnet which can provide exchange biasing with high-room-temperature thermal stability (Cain *et al.* 1987, Hasegawa *et al.* 1996, Kawawake *et al.* 1999, Sugita *et al.* 1999). In addition, the insulating nature of the oxide can be used to increase the magnetoresistance ratio of hybrid spin valves by specular reflection of electrons at the antiferromagnetic–ferromagnetic interface (Sakakima *et al.* 1999). This circumvents 'current shunting' found in systems with metallic antiferromagnets and enables one to reduce the shield gap in magnetic recording applications leading to enhanced sensitivity (Cain *et al.* 1987, Hasegawa *et al.* 1996, Kawawake *et al.* 1999, Sakakima *et al.* 1999, Sugita *et al.* 1999). A further obvious advantage of haematite is its excellent stability and corrosion resistance, unlike the Mn-based metallic antiferromagnets prevalent in many current applications.

The major problem with using polycrystalline haematite pinning layers lies with the rather low values of exchange bias that have been reported thus far (Hempstead *et al.* 1978, Cain *et al.* 1987, Layadi *et al.* 1987, Hasegawa *et al.* 1996, Sano *et al.* 1998, Kawawake *et al.* 1999, Sakakima *et al.* 1999, Sugita *et al.* 1999). Maximum values seem to lie in the range 6–40 Oe (for a ferromagnetic film thickness of about 100 Å) equivalent to about 0.01–0.04 erg cm⁻². It is worth noting that strong coercivity enhancements are often observed (Cain *et al.* 1987, Hasegawa *et al.* 1996) in these experiments, leading to the speculation that this material could be useful in terms of hard-magnet applications based on antiferromagnetic/ferromagnetic structures (Edelstein *et al.* 1999, Sort *et al.* 1999). Interestingly, attempts have been made to enhance the exchange bias by combining haematite with another antiferromagnet to produce composite antiferromagnets with higher exchange bias values (Fujikata *et al.* 1998, Kawawake *et al.* 1999).

The important point here is that the low values of exchange anisotropy energy have been reported for polycrystalline thin films (Hempstead *et al.* 1978, Cain *et al.* 1987, Layadi *et al.* 1987, Hasegawa *et al.* 1996, Fujikata *et al.* 1998, Sano *et al.* 1998, Kawawake *et al.* 1999, Sakakima *et al.* 1999, Sugita *et al.* 1999) which may not be single phase or have a bulk-like crystal structure (Sano *et al.* 1998). Note that polycrystallinity will inevitably result in a situation where some spins lie normal to (or at an angle to) the interfacial plane, an effect which is known to reduce exchange bias (Nogués *et al.* 1999). To the best of our knowledge there has been no study of exchange biasing by epitaxial haematite thin films. This is despite the fact that epitaxy has been demonstrated in thin films deposited by reactive evaporation (Bando *et al.* 1978) and molecular beam epitaxy (MBE) (Gao and Chambers 1997, Voogt 1998). Such films have even been used to study the Morin spin-flip transition in various crystalline orientations (Fuji *et al.* 1994) but no exchange biasing and no growth by sputter deposition have been attempted. In summary, it seems clear that an investigation of the sputtering conditions for high quality epitaxy of α -Fe₂O₃ layers is timely.

§2. EXPERIMENTAL DETAILS

The films were deposited on single-crystal sapphire (α -Al₂O₃) substrates to encourage epitaxy of the rhombohedral crystal structure. Note that the lattice mismatch is approximately 5.5%. The (0001) orientation was chosen so as to result in a structure with the spins in the interfacial plane at room temperature (above T_M) although it should be noted that epitaxy on (11 $\bar{2}$ 0) substrates was also possible. The substrates were cleaned chemically, then heated to 700°C and allowed to equilibrate and outgas for 10 min in a chamber with a base pressure below 1×10^{-7} Torr. The Fe sputtering target was then pre-sputtered in an Ar–O₂ mixture for 20 min prior to deposition. Films were deposited over a range of substrate temperature from ambient temperature up to 800°C and with O₂:Ar ratios from 0.65 mTorr O₂:20 mTorr Ar to 3 mTorr O₂:20 mTorr Ar. Note that the substrates were mounted on Cu foil to encourage uniform equilibration of the temperature. An in-plane field of about 100 Oe was applied during growth. Although the sputtering was performed at a constant power of 50 W in all cases, the deposition rate varied strongly with O₂ partial pressure.

§3. RESULTS AND DISCUSSION

Low temperature deposition at $T < 250^\circ\text{C}$ resulted in samples with mixed phases of Fe₃O₄ and γ -Fe₂O₃ at all O₂:Ar partial pressure ratios. Higher-temperature deposition with $300^\circ\text{C} < T < 800^\circ\text{C}$ resulted in single phase epitaxial growth as determined by the X-ray diffraction measurements presented below. The fact that we observe a clear dependence on substrate temperature, with lower substrate temperatures tending to favour lower oxygen content films is noteworthy. The opposite is true of reactive evaporation and MBE growth where single-phase Fe₂O₃ can only be achieved at low temperatures (less than 100°C) and low deposition rates, while the lower oxygen content Fe₃O₄ phase is available at higher temperatures. Single-phase α -Fe₂O₃ growth could be attained with O₂:Ar ratios from 1.6 mTorr O₂:20 mTorr Ar to 3.0 mTorr O₂:20 mTorr Ar. However, as mentioned earlier, increasing the O₂ partial pressure from 0.65 to 3 mTorr reduces the deposition rate by over an order of magnitude. A fairly low O₂ pressure of 2.0 mTorr was therefore chosen, which resulted in a deposition rate of about 0.6 \AA s^{-1} at a constant source to substrate distance.

Figure 1 shows the large-angle X-ray diffraction from a typical sample grown under the conditions described above, namely O₂ at 2.0 mTorr and 700°C. This is a θ - 2θ scan (see the schematic diagram in the inset of figure 3) with the scattering vector perpendicular to the sample plane and therefore probes crystalline coherence in the growth direction. The only observable peaks are from the c -axis substrate and the (0006) c -axis reflection of α -Fe₂O₃ at 39.30° compared with 39.28° for the literature bulk value (Blake *et al.* 1966). As is evident from figure 1, the α -Fe₂O₃ peak is very narrow. In fact the full width at half-maximum (FWHM) of only 0.2° demonstrates that the grain size is comparable with the thickness of the film, proving that the film is coherent in the growth direction. Moreover, close inspection of this peak (as shown in the inset of figure 1) reveals finite-size oscillations up to sixth order, indicating low surface roughness. Calculation of the film thickness from these oscillations results in a value of 400 Å, in good agreement with the reflectivity measurements presented below. Further evidence of the crystalline order in the growth direction is given by the transverse (θ) scan through the large-angle α -Fe₂O₃ (0006) reflection. The FWHM of the rocking curve is only 0.12° , which is exception-

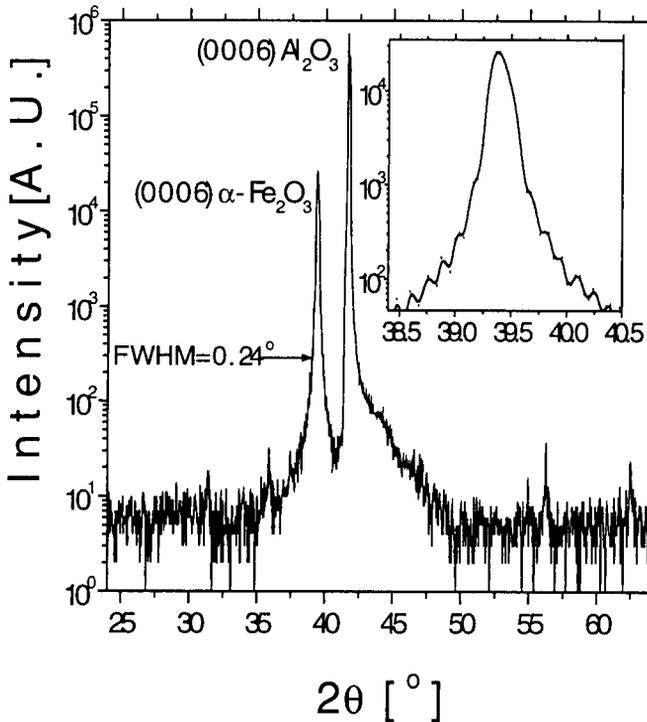


Figure 1. Large-angle X-ray diffraction (θ - 2θ scan with the scattering vector normal to the interface plane) on a representative sample as described in the text (A.U., arbitrary units). Cu K α radiation was employed. The inset shows a close up of the α -Fe₂O₃(0006) reflection, showing the finite-size oscillations. The scattering geometry is identical with that in figure 3 and is depicted in the inset of figure 3. Note that the FWHM of the transverse (θ) scan through the (0006) peak is only 0.12° .

ally low for a thin film sample. Note also that the miscut angle (with respect to the substrate) deduced from the X-ray scattering data is small, of the order of 0.3° .

The epitaxy in the sample plane was probed by performing in-plane grazing-incidence diffraction measurements as shown in figure 2. The two ' ϕ scans' shown in figures 2(a) and (b) correspond to the α -Fe₂O₃(110) and Al₂O₃(110) substrate in-plane reflections respectively. Here the scattering vector is in the sample plane as shown in the schematic diagram in figure 2. Commensurate peak positions for the substrate and film clearly demonstrate the simple epitaxial relationship between the two. Peak separations of 60° confirm the expected hexagonal crystal symmetry, while small FWHMs the order of 0.8° indicate low mosaic spread.

These film properties were found over the whole thickness range investigated, from 270 to more than 1500 Å. Moreover, almost identical structural properties were observed from 300 up to 800°C. To the best of our knowledge these films have the lowest large-angle rocking-curve FWHMs reported in the literature, with in-plane widths comparable with those of the best MBE films available.

Grazing-incidence reflectivity was also performed to gain information on the thickness and surface roughness of the films, as shown in figure 3. In this geometry (see the schematic diagram in figure 3) the scattering vector is normal to the sample surface and the height fluctuations in the growth direction are probed. The θ - 2θ scan

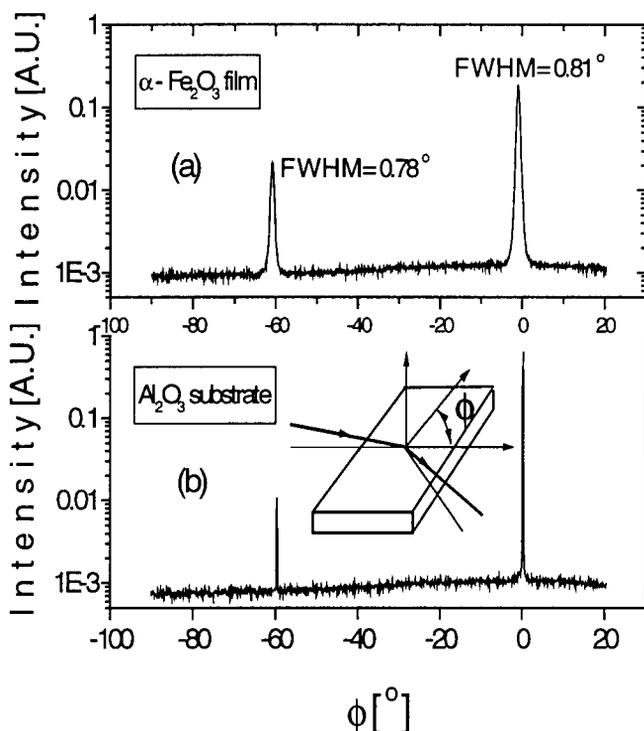


Figure 2. In-plane X-ray diffraction (ϕ scan with the scattering vector in the sample plane) of a representative sample as described in the text (A.U., arbitrary units). Cu K α radiation was employed: (a) the α - Fe_2O_3 diffraction data; (b) the Al_2O_3 substrate data. The FWHMs of the film peaks are of the order of 0.8° . The schematic inset depicts the scattering geometry. Here the angle between the incident beam and the sample plane is set at 0.4° , which is just above the critical angle for α - Fe_2O_3 of 0.33° . The sample is then rotated around the normal to the sample surface. Note that the thick lines are the X-ray beam directions, while the fine lines are directions in the plane.

shows many (more than ten) finite size oscillations out to $q_z > 0.30 \text{ \AA}^{-1}$, indicating a very smooth surface over the length scales probed in the grazing-incidence geometry (approximately 100 to 1000 \AA (Schuller *et al.* 1999)). Quantitative modelling of the profile was performed by comparison with the recursive simulation SUPREX (SUPerlattice REFinement by X-ray) model (Schuller 1980, Sevenhans *et al.* 1986, Fullerton *et al.* 1992). The solid curve in figure 3 shows the result of such a simulation with a film thickness of 360 \AA and a roughness of only 0.3 \AA . Such low roughness values should be treated with caution although it is clear that the sample surface is smooth over the long lateral length scale probed in this geometry. Note that the existence of the finite size oscillations around the large-angle haematite peak shown in figure 1 and discussed above indicates that the surface also remains smooth over shorter lateral length scales.

Unlike the FWHMs of the peaks in figures 1 and 2, the roughness deduced from the grazing-incidence reflectivity profile (figure 3) *does* depend on substrate temperature in the range $300^\circ\text{C} < T < 800^\circ\text{C}$, with 600 – 700°C being the optimum range. In other words, as the temperature is varied between 300 and 800°C , we are able to alter the surface roughness while the crystalline coherence and mosaicity in the growth

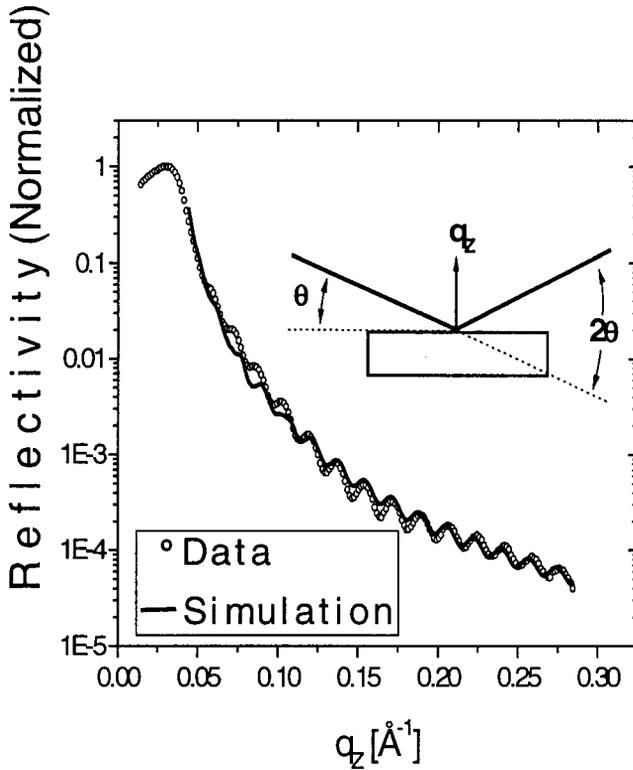


Figure 3. Grazing incidence X-ray reflectivity profile (small-angle θ - 2θ scan with the scattering vector normal to the interface plane) of a representative sample as described in the text. Cu $K\alpha$ radiation was employed. The solid curve is based on a simulation with a film thickness of 360 \AA and a roughness of 0.3 \AA . The schematic inset depicts the scattering geometry.

direction remain unchanged. This may prove to be a useful property in terms of examining the dependence of exchange bias on interface disorder as in the work by Leighton *et al.* (1999).

A final piece of structural characterization was obtained by reflection high-energy electron diffraction (RHEED). For these measurements, samples were removed from the growth chamber and transferred in air to an ultrahigh-vacuum chamber. The samples were then annealed at 400°C (note that this is well below the growth temperature of 700°C , making a structural alteration unlikely) for 5 min at pressures below 1×10^{-9} Torr. RHEED images consisted of sharply defined streaks which revealed the same crystal symmetry as in plane X-ray scattering, on rotation of the sample. The intensity profile through the specular streak is shown in figure 4 for the same sample as in figures 1–3, with a Lorentzian fit. The FWHM was found to be only 0.15 \AA^{-1} , which suggests a large lateral coherence length. In fact this is approaching our instrumental limit (Kim *et al.* 1997, Choi *et al.* 1999).

Rf superconducting quantum interference device (SQUID) magnetometry on these films showed a susceptibility below the sensitivity of the device (3×10^{-8} emu), placing an upper limit on uncompensated interface spins or bulk Fe clusters. Such effects have been reported in a previous publication on thin-film α - Fe_2O_3 layers (Dimitrov *et al.* 1997), which essentially showed ferromagnetic

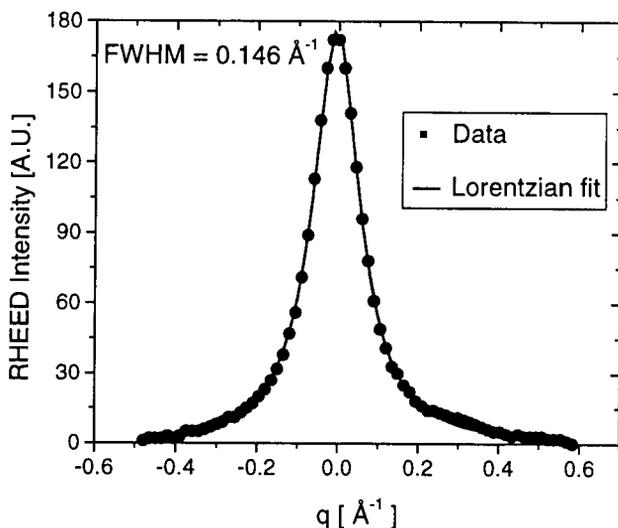


Figure 4. RHEED intensity profile through the specular [00] streak (A.U., arbitrary units). The solid curve is a Lorentzian fit with a FWHM of 0.146 \AA^{-1} . The data were taken at a beam voltage of 10 kV.

behaviour. Our measurements are consistent with bulk data where a susceptibility of only $2 \times 10^{-5} \text{ emu g}^{-1} \text{ Oe}^{-1}$ is expected at $T = 300 \text{ K}$ (Morrish 1994, p. 59). This is equivalent to a moment of $1.2 \times 10^{-8} \text{ emu}$ in a 10 kOe field for a film 400 \AA thick and of area 1 cm^2 , well below the SQUID's sensitivity.

§4. SUMMARY AND CONCLUSIONS

In summary we have presented the details of reactive dc magnetron sputtering of epitaxial smooth thin films of haematite for exchange bias studies. Optimized sputtering conditions were discussed together with the results of the characterization of the films. Large-angle rocking-curve widths of the order of 0.12° have been achieved, as well as a clear demonstration of in-plane epitaxy.

ACKNOWLEDGEMENTS

We would like to thank S. Kim for assistance with RHEED measurements and for illuminating discussions. This work was supported by the US Department of Energy, BES-DMS, under contract W-7405-Eng-36.

REFERENCES

- BANDO, Y., HORII, S., and TAKADA, T., 1978, *Jap. J. appl. Phys.*, **17**, 1037.
 BERKOWITZ, A. E., and TAKANO, K., 1999, *J. Magn. matgn. Mater.*, **200**, 552.
 BLAKE, R. L., HESSERICK, R. E., ZOLTAL, T., and FINGER, L. W., 1966, *Am. Mineral.*, **51**, 123.
 CAIN, W. C., MEIKLEJOHN, W. H., and KRYDER, M. H., 1987, *J. appl. Phys.*, **61**, 4170.
 CHOI, J. M., KIM, S., SCHULLER, I. K., PAIL, S. M., and WHANG, C. N., 1991, *J. Magn. magn. mater.*, **191**, 54.
 CREER, K. M., HEDLEY, I. G., and O'REILLY, W., 1980, *Magnetic Oxides*, edited by D. J. Craik (London: Wiley), p. 649.
 DIENY, B., SPERIOSU, V., PARKIN, S. S. P., GURNEY, B. A., WILHOIT, D. R., and MAURI, D., 1991, *Phys. Rev. B*, **43**, 1297.

- DIMITROV, D. V., HADJIPANAYIS, G. C., PAPAETHYMIU, V., and SIMOPOULOS, A., 1997, *Magnetic Hysteresis in Novel Magnetic Materials*, edited G. C. Hadjipanayis (Dordrecht: Kluwer), p. 517.
- EDELSTEIN, A. S., KODAMA, R. H., MILLER, M., BROWNING, V., LUBITZ, P., CHANG, S. F., and SIEBER, H., 1999, *Appl. Phys. Lett.*, **74**, 3872.
- FUJII, T., TAKANO, M., KATANO, R., ISOZUMI, Y., and BANDO, Y., 1994, *J. Magn. magn. Mater.*, **135**, 231.
- FUJIKATA, J., HAYASHI, K., SAITO, M., and NAKADA, M., 1998, *IEEE Trans. Magn.*, **34**, 954.
- GAO, Y., and CHAMBERS, S. A., 1997, *J. Cryst. Growth*, **174**, 446.
- HASEGAWA, N., MAKINO, A., KOIKE, F., and IKARASHI, K., 1996, *IEEE Trans. Magn.*, **32**, 4618.
- HEMPSTEAD, R. D., KRONGELB, S., and THOMPSON, D. A., 1978, *IEEE Trans. Magn.*, **14**, 521.
- KAWAWAKE, Y., SUGITA, Y., SATOMI, M., and SAKAKIMA, H., 1999, *J. appl. Phys.*, **85**, 5024.
- KIM, S., SUHL, H., and SCHULLER, I. K., 1997, *Phys. Rev. Lett.*, **78**, 322.
- LAYADI, A., CAIN, W. C., LEE, J.-W., and ARTMAN, J. O., 1987, *IEEE Trans. Magn.*, **23**, 2993.
- LEIGHTON, C., NOGUÉS, J., SUHL, H., and SCHULLER, I. K., 1999, *Phys. Rev. B*, **60**, 12837.
- MEIKLEJOHN, W. H., and BEAN, C. P., 1956, *Phys. Rev.*, **102**, 1413.
- MORIN, F. J., 1950, *Phys. Rev.*, **78**, 819.
- MORRISH, A. H., 1994, *Canted Antiferromagnetism* (Singapore: World Scientific).
- NOGUÉS, J., MORAN, T. J., LEDERMAN, D., SCHULLER, I. K., and RAO, K. V., 1999, *Phys. Rev. B*, **59**, 6984.
- NOGUÉS, J., and SCHULLER, I. K., 1999, *J. Magn. magn. Mater.*, **192**, 203.
- SAKAKIMA, H., SUGITA, Y., SATOMI, M., and KAWAWAKE, Y., 1999, *J. Magn. magn. Mater.*, **198-199**, 9.
- SANO, M., ARAKI, S., OHTA, M., NOGUCHI, K., MORITA, H., and MATSUZAKI, M., 1998, *IEEE Trans. Magn.*, **34**, 372.
- SCHULLER, I. K., 1980, *Phys. Rev. Lett.*, **44**, 1597.
- SCHULLER, I. K., KIM, S., and LEIGHTON, C., 1999, *J. Magn. magn. Mater.*, **200**, 571.
- SEVENHANS, W., GIJS, M., BRUYNSERAEDE, Y., HOMMA, H., and SCHULLER, I. K., 1986, *Phys. Rev. B*, **34**, 5955.
- SORT, J., NOGUÉS, J., AMILS, X., SURINACH, S., MUÑOZ, J. S., BARÓ, M. D., 1999, *Appl. Phys. Lett.*, **75**, 3177.
- SUGITA, Y., KAWAWAKE, Y., SATOMI, M., SAKAKIMA, H., 1999, *IEEE Trans. Magn.*, **35**, 2961.
- VOOGT, F. C., 1998, PhD Thesis, University of Groningen.