

Contents lists available at [ScienceDirect](http://ScienceDirect)

# Journal of Magnetism and Magnetic Materials

journal homepage: [www.elsevier.com/locate/jmmm](http://www.elsevier.com/locate/jmmm)

## Four-fold magnetic anisotropy in a Co film on MgO(0 0 1)

M.J.M. Pires\*, A.A.C. Cotta, M.D. Martins, A.M.A. Silva, W.A.A. Macedo

Serviço de Nanotecnologia, Centro de Desenvolvimento da Tecnologia Nuclear, 31270-901 Belo Horizonte, MG, Brazil

### ARTICLE INFO

#### Article history:

Received 6 August 2010

Received in revised form

21 October 2010

Available online 7 November 2010

#### Keywords:

Magnetic anisotropy

Magnetic thin film

### ABSTRACT

The development of devices based on magnetic tunnel junctions has raised new interests on the structural and magnetic properties of the interface Co/MgO. In this context, we have grown ultrathin Co films ( $\leq 30$  Å) by molecular-beam epitaxy on MgO(0 0 1) substrates kept at different temperatures ( $T_S$ ). Their structural and magnetic properties were correlated and discussed in the context of distinct magnetic anisotropies for Co phases reported in the literature. The sample characterization has been done by reflection high energy electron diffraction, magneto-optical Kerr effect and ferromagnetic resonance. The main focus of the work is on a sample deposited at  $T_S = 25$  °C, as its particular way of growth has enabled a bct Co structure to settle on the substrate, where it is not normally obtained without specific seed layers. This sample presented the best crystallinity, softer magnetic properties and a four-fold in-plane magnetic anisotropy with Co  $\langle 1 1 0 \rangle$  easy directions. Concerning the samples prepared at  $T_S = 200$  and  $500$  °C, they show fcc and polycrystalline structures, respectively and more intricate magnetic anisotropy patterns.

© 2010 Elsevier B.V. Open access under the [Elsevier OA license](http://www.elsevier.com/locate/elsevier).

### 1. Introduction

Different materials employing metastable cubic phases of cobalt have acquired great relevance for several applied and basic researches along the last decades [1–5]. Cu, ZnSe and GaAs are often used as substrates to grow the Co cubic phases, fcc in the case of Cu [6–9] and bcc in the other two cases [10–13]. Actually epitaxial thin films of such materials are not exactly cubic but tetragonal distorted structures (fct or bct), although the main magnetic aspects can be well described by models assuming cubic structures. In bulk fcc and in films with fct structure similar to the bulk, the easy directions for the magnetization are [1 1 1] and [1 1 0], respectively, [7,14], while in systems with bcc or bct structure distinct directions can be found [12,13].

MgO, an insulating, stable and non-interactive material, is largely employed for the growth of magnetic thin films and became very important due to the close lattice match with Fe (45° oriented) and with GaAs [15,16], since Fe films and GaAs have already a wide variety of applications, mainly in the magnetic and microelectronic technologies.

The deposition of Co films on MgO single crystals by sputtering and molecular-beam epitaxy systems was already significantly explored seeking different properties [14,17–23], and a large amount of distinct structures has been obtained, including both cubic/tetragonal [14,18,19] and hexagonal [17,18,21] unit cells. The large misfit between MgO and cubic Co lattices ( $\sim 16\%$ ) is not favorable for the

epitaxial growth of Co on MgO. There are some reports on the pseudomorphic growth of fcc Co on MgO(1 1 0) [20,24] and on MgO(0 0 1) [14,19,23,24], but in most of the cases [14,19,20,24] a textured film was obtained with a significant in-plane uniaxial magnetic anisotropy. Even in the best samples studied in those works [14] the crystal quality of the fcc Co is argued to be poor when compared with Fe–Co alloys deposited under the same conditions. The formation of 90° twinned hcp domains in the Co films deposited on MgO(0 0 1) has also been reported [18,24], and in this case a quite regular four-fold in-plane magnetic anisotropy was observed by Goryunov et al. [18]. Nevertheless the Co/MgO interface has recently acquired new interests as a giant tunneling magnetoresistance was observed in Co/MgO/Fe and in Co/MgO/Co junctions with bcc Co [3,4], confirming theoretical predictions [2,5]. The discussion about a possible enhancement of the magnetization of Co at interfaces has deserved also new studies [17,25]. For these reasons the growth and the detailed characterization of epitaxial Co/MgO structures are currently important under several aspects.

In this context, we have prepared ultrathin ( $\leq 30$  Å) Co films on MgO(0 0 1) single crystals with magnetic properties as soft as fcc Co epitaxially grown on the Cu(0 0 1) single crystals. The structure of the samples was analyzed by reflection high energy electron diffraction (RHEED) during the deposition, and the magnetic behavior has been analyzed by magneto-optical Kerr effect (MOKE) and ferromagnetic resonance (FMR). FMR results showed a clear four-fold in-plane magnetic anisotropy for a sample deposited at 25 °C, which is compatible with an in-plane squared structure of the Co. The easy axes deduced from this result are parallel to the Co  $\langle 1 1 0 \rangle$  directions. The establishment of these easy axes is

\* Corresponding author.

E-mail address: [manoeljmp@gmail.com](mailto:manoeljmp@gmail.com) (M.J.M. Pires).

related to the huge strain present in the film deposited at 25 °C, which probably leads its structure beyond the Bain transition from fcc to bcc lattices.

## 2. Experimental

The samples were prepared in a VG ultrahigh vacuum chamber equipped with RHEED and low energy electron diffraction (LEED) optics, a CLAM 2 analyzer for X-ray photoelectron spectroscopy (XPS), and Oxford Applied Research e-beam evaporators. The base pressure was  $1.4 \times 10^{-10}$  mbar. High purity Co (99.995%, Alfa Aesar) was evaporated on MgO(0 0 1) substrates using an e-beam evaporator. The MgO single crystals surface was previously cleaned in UHV by annealing at temperatures between 500 and 700 °C for 2 h, and the surface structure was checked by LEED and XPS. The typical evaporation rates were between 1 and 2 Å/min, as measured by a quartz microbalance. The pressure during the evaporation stayed below  $3.0 \times 10^{-9}$  mbar. Samples labeled F1, F2 and F3, with a nominal thickness of 30 Å, were deposited on the MgO substrate kept at  $T_s=25, 200$  and 500 °C, respectively.

Besides RHEED and XPS, setups for FMR (Varian E-12; 9.5–9.7 GHz) and longitudinal MOKE measurements were employed for the sample characterization.

## 3. Results

### 3.1. Structural properties

Fig. 1 (top) shows the typical [24,26] RHEED pattern obtained for the MgO(0 0 1) substrate immediately before the deposition of

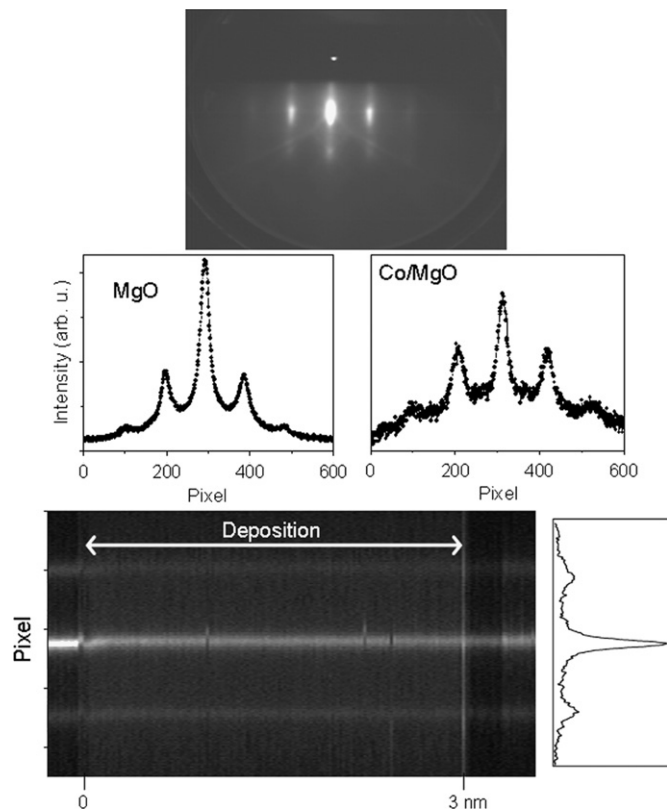


Fig. 1. Top: typical RHEED patterns of the MgO substrates for the [1 0 0] azimuth; middle: RHEED profiles obtained before and after the deposition of 30 Å Co at  $T_s=25$  °C (sample F1); bottom: RHEED profile map along the deposition of the Co film F1. The initial part of the map corresponds to the clean substrate.

the Co films. The well defined pattern and the Kikuchi lines show a smooth and clean surface.

RHEED streaks were clearly observed during the whole deposition of all samples. Fig. 1 also presents RHEED profiles and a map of the deposition of sample F1. For  $T_s=25$  °C (film F1), only slight alterations in the pattern occur during the process, but no additional diffraction spots or streaks appear, and the streaks do not become discrete. At the final of the deposition, the distance between the streaks remains approximately the same as that of the substrate. All these facts indicate that the initial structure of the film is maintained and follows closely one of the fcc substrate [27].

The influence of carbon adsorbed at the surfaces of MgO crystals on the growth process of Fe and Co films has been recently investigated by Sicot et al. [25]. They show a  $c(2 \times 2)$  surface reconstruction for thin Fe layer and alterations in the surface reactivity associated to the C contamination. For our samples, we cannot rule out such an influence, as small amounts of C has been detected by the XPS analysis. However, no reconstruction has been observed with both the electron diffraction techniques (RHEED and LEED) for any of the MgO substrates and during the Co deposition. The signal of C was always very small for a reliable quantification, and at the end of the Co deposition no contaminant has been detected in any of the samples.

Fig. 2 shows the evolution of the lateral lattice parameter along the growth of the films, as determined from the distance between the RHEED streaks. For sample F2 there is a decrease of about 14% in the parameter and this value is reached around the thickness of 5 Å. For sample F3 the broadening of the diffraction patterns does not permit a satisfactory determination of the parameter through the whole process. The lattice parameter for bulk fcc  $\alpha$ -Co (3.54 Å) is about 16% smaller than that of MgO (4.21 Å), then it can be said that the RHEED results for samples F2 are compatible with films with lateral lattice parameter of the same order of bulk fcc Co, distinctly to what is observed for sample F1, which roughly presents the same parameter along the whole deposition. In fact, considering the conservation of the typical unit-cell volume of fcc Co and the MgO parameter for the in-plane lattice distances, F1 has a  $c/a$  ratio of about 0.64, which is beyond the Bain transformation from fcc to bcc structures [28,29]. The bct cell formed in this way has a  $c'/a'$  ratio of 1.05 with lattice parameters around 3 Å, only about 6% larger than the one obtained by Prinz for bcc Co on GaAs [12].

Typical RHEED images for the samples and the substrates are presented in Fig. 3. It can be observed that the crystal quality of the films decreases with the increase in growth temperature. The

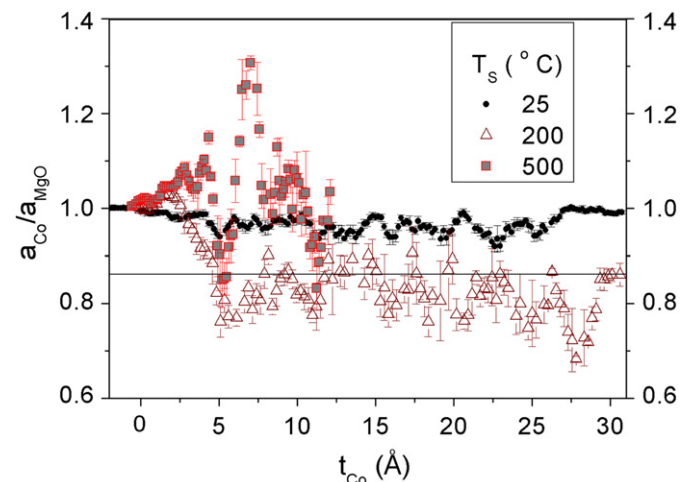
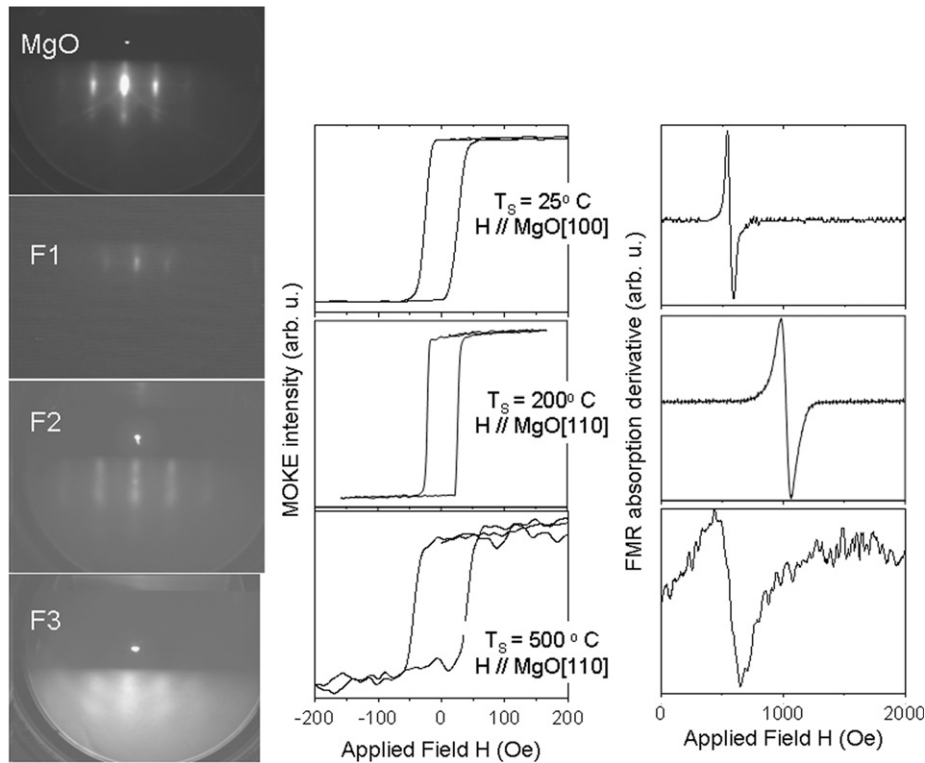


Fig. 2. Evolution of the lateral lattice parameter of the Co films, as determined from the RHEED measurements. F1 presents practically the same initial and final values. The horizontal line highlights the final value for this parameter in sample F2.



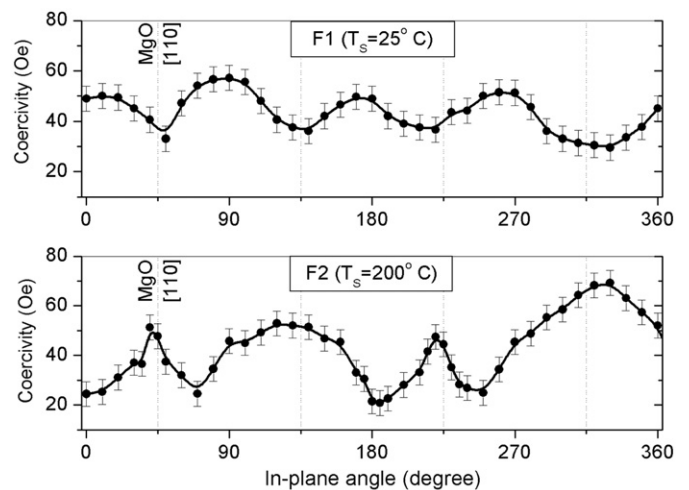
**Fig. 3.** RHEED patterns at the MgO[1 0 0] azimuth (left); longitudinal MOKE hysteresis loops (center); FMR spectra (right) for the Co ultrathin films prepared at different temperatures ( $T_s$ ).

results for sample F3 points to a polycrystalline structure [15], while for samples F1 and F2 it can be said that the films present large atomically flat terraces. Concerning the intensity of the streaks, it decreases almost monotonically along the deposition of films F1 and F2 (more rapidly in the first 4 Å of equivalent thickness). This behavior is compatible with the Volmer–Weber mode of growth. For the film F3, the poor quality of the patterns does not allow such an analysis.

### 3.2. Magnetic properties

MOKE hysteresis loops obtained at room temperature are presented in Fig. 3. Samples F1 and F2 are expressively soft magnetic films, as the coercivities of the order of 50 Oe indicate. Similar results were already reported for fcc Co(0 0 1) epitaxially grown on fcc Cu(0 0 1) single crystals [6–9,30], which have a lattice parameter of 3.62 Å, a value very close to that of bulk fcc Co (a misfit < 2% compared with 16% between MgO and fcc Co). For Co films on MgO, the results available present coercivities between 100 and 400 Oe [20,21,24,26]. The soft magnetic properties of our samples are confirmed by in-plane FMR spectra obtained also at room temperature (Fig. 3), which present rather small linewidths for samples F1 and F2. These linewidths are of the same order as that of measured in fcc Co(0 0 1) films grown on the Cu(0 0 1) single crystals [31,32] and, again, expressively smaller than the values already found for Co films deposited on the MgO(0 0 1) [18,23]. The reduced FMR linewidth is directly related to the crystalline quality of the samples [7,31].

Clear MOKE signals (not shown) have been detected at room temperature in a wedged sample prepared under the same conditions of sample F1 from the nominal thickness of 4–30 Å Co. This result is compatible with what is obtained for Co on Cu(0 0 1), where for films with thicknesses around and above 1.7 Å, the Curie temperature is already above 300 K [6–8].



**Fig. 4.** MOKE coercivity as a function of the angle in the (0 0 1) plane for samples F1 and F2.

In-plane angular dependent longitudinal MOKE was measured for all samples. For samples F1 and F2 the easy directions correspond to the MgO<1 0 0> and <1 1 0> directions, respectively (Fig. 4). However, sample F1 is the only one presenting a clear and regular symmetry pattern, a four-fold pattern. This pattern is slightly perturbed by a small uniaxial contribution along the MgO[1 1 0] direction. A tendency for a uniaxial magnetic anisotropy could be noted in the results for samples F2 and F3, although in F2 a four-fold anisotropy is also present. For these two samples the different anisotropy contributions could not be clearly unscrambled. In some field orientations the quality of the MOKE signal is poor, which makes the identification of the easy axes questionable. Both uniaxial contribution and surface effects affect the MOKE results.

The four-fold magnetic anisotropy of sample F1 is a strong indication of a squared in-plane crystalline structure, which can be reflecting a cubic or tetragonal unit cell. To check this magnetic behavior, angle dependent FMR measurements were conducted for this sample. The in-plane angular variation of the external magnetic field for resonance ( $H_{\text{res}}$ ) is shown in Fig. 5. A rather regular four-fold pattern is clearly seen, confirming the MOKE results. The small influence of the uniaxial contribution can be noted in the different values of  $H_{\text{res}}$  at the minima at  $0^\circ$  and  $180^\circ$  when compared with the values at  $90^\circ$  and  $270^\circ$ .

The  $H_{\text{res}}$  curve of Fig. 5 has been fitted employing the usual model [7,31]. The magnetocrystalline, Zeeman, and the shape energy contributions were used in the free energy density expression. Following the notation from Farle [31], the magnetocrystalline contribution has been set as

$$F_{\text{MC}} = -\frac{1}{2}K_{4\parallel} \frac{1}{4} [3 + \cos(4\varphi)] \sin^4(\theta) - \frac{1}{2}K_{4\perp} \cos^4(\theta)$$

where  $K_{4\parallel}$  and  $K_{4\perp}$  are the fourth-order terms of the magnetic anisotropies parallel and perpendicular to the film plane, and  $\theta$  and  $\varphi$  the polar and azimuthal coordinates of the magnetization, respectively.  $\varphi$  is measured from the MgO[1 0 0] direction for experimental convenience. In this framework, the  $H_{\text{res}}$  curve can be fitted letting the  $g$  factor,  $2K_{4\parallel}/M_S$ , and  $4\pi M_{\text{eff}} = 4\pi M_S - 2K_2/M_S$  as free parameters.  $K_2$  and  $M_S$  are the second-order terms of the perpendicular anisotropy and the saturation magnetization, respectively. The surface contributions to the out-of-plane anisotropy are imbedded in  $K_2$ .

This approach leads to the following results:  $g = 2.16 \pm 0.01$ ,  $2K_{4\parallel}/M_S = 169 \pm 9$  Oe and  $4\pi M_{\text{eff}} = 14.4 \pm 0.2$  kG. Considering the magnetization of saturation as  $\sim 1400$  emu/cm<sup>3</sup>, value normally found in Co, this value of  $2K_{4\parallel}/M_S$  corresponds to  $K_{4\parallel} = 1.2 \times 10^5$  erg/cm<sup>3</sup>, and  $4\pi M_{\text{eff}} = 14.4 \pm 0.2$  kG corresponds to  $K_2 = -2.2 \times 10^6$  erg/cm<sup>3</sup>. These results could be used in the resonance condition at the perpendicular configuration for the determination of the term  $K_{4\perp}$ , but our maximum field available was 20 kOe and it was not possible to detect the resonance line in a range of  $4^\circ$  around the perpendicular configuration. Considering the results for the remaining angular range,  $K_{4\perp}$  can be estimated as  $-1.7 \times 10^6$  erg/cm<sup>3</sup>, although the lack of measurements at the perpendicular configuration makes this result a poor estimate. However, since the Co lattice in this sample is laterally expanded, a drastic compression is expected in the perpendicular direction, hence distinct  $K_{4\parallel}$  and  $K_{4\perp}$  are also expected.

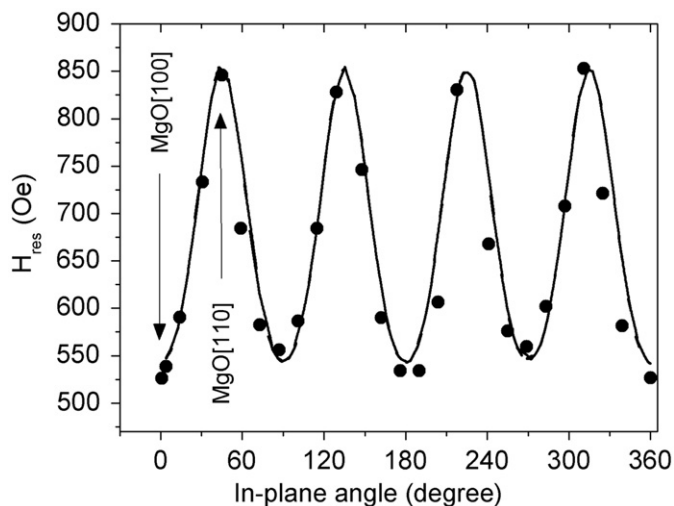


Fig. 5. (0 0 1) in-plane angular variation of the external field for resonance and the corresponding best fit for sample F1.

#### 4. Discussion and conclusions

In the available reports of molecular-beam epitaxy growth of fcc Co films on MgO with lattice parameter close to that of bulk fcc Co [20,22,24], the samples were prepared with the substrate held at temperatures between 300 and 350 °C. Our results for sample F2 agree with these findings. The other two growth temperatures we have tested led to other two distinct regimes of growth, since the substrates have been adequately prepared. At 25 °C an epitaxial match occurs, at least for ultrathin films, leading to a film with high crystalline quality. At 500 °C this epitaxial growth does not occur, resulting in a polycrystalline film. There are other works [14,23] on the growth of fcc Co films on MgO with lattice parameter close to that of bulk fcc Co, but those films are far thicker than the ones presented here, and even thicker than the effective bulk limit ([33] and references therein). In these cases, deposition temperatures above 200 °C seem to result in similar growths.

The value obtained for the  $g$  factor in sample F1 is in the range normally found in cubic Co for different systems [7,31,32]. Regarding the value of  $K_2$ , the negative signal agree with the fact that the easy direction is in the film plane. Furthermore its magnitude is one order of magnitude smaller than that found in fcc Co (10 ML)/Cu(0 0 1) [7], which means, it can be easier for surface effects to overcome the natural tendency for an in-plane easy axis of magnetization in the case of epitaxial Co/MgO than in Co/Cu.

The rather regular magnetic anisotropy pattern we observed for sample F1 is directly related to the best crystalline quality of this sample, permitting the determination of the in-plane fourth-order magnetocrystalline field. The value found for this parameter is of the same magnitude of what is found in bulk fcc Co and in Co films, where the lattice parameter is similar to the bulk value [7,31], but the signal is the opposite. Considering that the film has a bct structure resulting from the Bain transition, the Co[1 0 0] is collinear with the MgO[1 1 0] direction, and therefore the opposite signal for  $K_{4\parallel}$  corresponds to Co <1 1 0> easy axes (in-plane).

Burkert et al. [29] published first principles calculation of the magnetic anisotropy of Co along the Bain path, but only for the second-order out-of-plane anisotropy constant. They found large positive values for this constant in the region, which corresponds to the  $c/a$  of sample F1. We found small negative values for  $K_{4\perp}$ , but the comparison with their calculation cannot be done directly as our value is a poor estimate, as mentioned in the previous section, and because the contributions to  $K_2$  cannot be disentangled in this approach.

The signal of  $K_{4\parallel}$  in bcc Co films is a controversial subject involving the interplay between the magnetocrystalline and the surface/interface contributions for the anisotropy and the mixture of crystalline phases [13,34]. Nevertheless, in sample F1 we can say that the four-fold contribution attributed to the magnetocrystalline anisotropy is clearly dominant over the uniaxial one, and the whole set of results indicate a bct film with in-plane <1 1 0> easy axes.

#### Acknowledgments

The financial support from the agencies MCT/CNPq, CAPES and FAPEMIG is gratefully acknowledged. The authors are grateful to Photothermics and Magnetic Resonance group of the IFGW-UNICAMP for kindly permitting the use of the FMR set up.

#### References

- [1] A.D.C. Viegas, J. Geshev, J.E. Schmidt, E.F.J. Ferrari, J. Appl. Phys. 83 (1998) 7007.
- [2] X-G. Zhang, W.H. Butler, Phys. Rev. B 70 (2004) 172407.

- [3] S. Yuasa, T. Katayama, T. Nagahama, A. Fukushima, H. Kubota, Y. Suzuki, K. Ando, *Appl. Phys. Lett.* 87 (2005) 222508.
- [4] S. Yuasa, A. Fukushima, H. Kubota, Y. Suzuki, K. Ando, *Appl. Phys. Lett.* 89 (2006) 042505.
- [5] M. Ležaić, M. Ph Mavropoulos, S. Blügel, *Appl. Phys. Lett.* 90 (2007) 082504.
- [6] C.M. Schneider, P. Bressler, P. Schuster, J. Kirschner, J.J. de Miguel, R. Miranda, *Phys. Rev. Lett.* 64 (1990) 1059.
- [7] B. Heinrich, J.F. Cochran, M. Kowalewski, J. Kirschner, Z. Celinski, A.S. Arrot, K. Myrtleç, *Phys. Rev. B* 44 (1991) 9348.
- [8] P. Pouloupoulos, P.J. Jensen, A. Ney, J. Lindner, K. Baberschke, *Phys. Rev. B* 65 (2002) 064431.
- [9] Y. Chan, N. Jih, C. Peng, C. Chuang, T.H. Lee, J.C.A. Huang, Y.J. Hsu, D.H. Wei, *J. Magn. Magn. Mater.* 310 (2007) e762.
- [10] C.J. Gutierrez, G.A. Prinz, J.J. Krebs, M.E. Filipkowski, V.G. Harris, W.T. Elam, *J. Magn. Magn. Mater.* 126 (1993) 232.
- [11] B.T. Jonker, G.A. Prinz, *J. Appl. Phys.* 69 (1991) 5676.
- [12] G.A. Prinz, *Phys. Rev. Lett.* 54 (1985) 1051.
- [13] X.Y. Xu, L.F. Yin, D.H. Wei, C.S. Tian, G.S. Dong, X.F. Jin, *Phys. Rev. B* 77 (2008) 052403.
- [14] Th. Mühge, Th. Zeidler, Ch. Morawe, N. Metoki, H. Zabel, *J. Appl. Phys.* 77 (1995) 1055.
- [15] C.M. Boubeta, J.L. Costa-Krämer, A. Cebollada, *J. Phys., Condens. Matter* 15 (2003) R1123.
- [16] G. Fahsold, A. Priebe, A. Pucci, *Appl. Phys. A* 73 (2001) 39.
- [17] M. Nishikawa, E. Kita, T. Erata, A. Tasaki, *J. Magn. Magn. Mater.* 126 (1993) 303.
- [18] Yu.V. Goryunov, M.G. Khusainov, I.A. Garifullin, F. Schreiber, J. Pelzl, Th. Zeidler, K. Bröhl, N. Metoki, H. Zabel, *J. Magn. Magn. Mater.* 138 (1994) 216.
- [19] M. Hashimoto, H. Qiu, T. Ohbuchi, M. Adamik, H. Nakai, A. Barna, P.B. Barna, *J. Cryst. Growth* 166 (1996) 792.
- [20] C.K. Lo, Y. Liou, C.P. Chang, I. Klık, Y.D. Yao, J.C.A. Huang, *Appl. Phys. Lett.* 68 (1996) 2155.
- [21] H. Sato, T. Miyazaki, *J. Magn. Magn. Mater.* 177–181 (1998) 1197.
- [22] C.K. Lo, I. Klık, Y. Liou, C.P. Chang, C.S. Yang, Y.D. Yao, *J. Magn. Magn. Mater.* 177–181 (1998) 1257.
- [23] V.C. Santos, A.A.R. Fernandes, E.E. Fullerton, C.A. Ramos, *Mater. Sci. Forum* 302–303 (1999) 76.
- [24] Y. Nukaga, M. Ohtake, M. Futamoto, F. Kirino, N. Fujita, N. Inaba, *IEEE Trans. Magn.* 45 (2009) 2519.
- [25] M. Sicot, S. Andrieu, C. Tiusan, F. Montaigne, F. Bertran, *J. Appl. Phys.* 99 (2006) 08D301.
- [26] S.G. Wang, C. Wang, A. Kohn, S. Lee, J.P. Goff, L.J. Singh, Z.H. Barber, R.C.C. Ward, *J. Appl. Phys.* 101 (2007) 09D103.
- [27] T. Tanabe, R. Buckmaster, T. Ishibashi, T. Wadayama, A. Hatta, *Surf. Sci.* 472 (2001) 1.
- [28] F. Milstein, Elastic stability criteria and structural bifurcations in crystals under load, in: S. Yip (Ed.), *Handbook of Materials Modeling*, Springer, Dordrecht, 2005, pp. 1251–1260.
- [29] T. Burkert, O. Eriksson, P. James, S.I. Simak, B. Johansson, L. Nordström, *Phys. Rev. B* 69 (2004) 104426; T. Burkert, O. Eriksson, P. James, S.I. Simak, B. Johansson, L. Nordström, *Phys. Rev. B* 70 (2004) 139901(E).
- [30] Q. Jiang, H.-N. Yang, G.-C. Wang, *Surf. Sci.* 373 (1997) 181.
- [31] M. Farle, *Rep. Prog. Phys.* 61 (1998) 755.
- [32] J. Lindner, K. Baberschke, *J. Phys., Condens. Matter* 15 (2003) R193.
- [33] G.Y. Guo, D.J. Roberts, G.A. Gehring, *Phys. Rev. B* 59 (1999) 14466.
- [34] X. Xu, L. Yin, G. Dong, X. Jin, *Phys. Rev. B* 80 (2009) 092405.