Structural tuning of the magnetic behavior in spinel-structure ferrite thin films

G. Hu,[1] J. H. Choi,[2] C. B. Eom,[2] V. G. Harris,[3] and Y. Suzuki[1]

[1]*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853*

[2]*Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 22208*

[3]*Naval Research Laboratory, Washington, DC 20375-5000*

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Epitaxial cobalt ferrite thin films provide a model system for understanding the magnetic properties of spinel structure ferrite *thin films*. We demonstrate that the anomalous magnetic behavior, observed in our antiphase-boundary-free films, can be explained in terms of cation distribution and lattice distortions. The magnetic anisotropy is a delicate balance between strain anisotropy, due to internal lattice strain or equivalent external strain effects, and magnetocrystalline anisotropy, due to cation distribution. By annealing the cobalt ferrite thin films and hence varying the cobalt cation distribution among the tetrahedral and octahedral sites and the strain state of the films, we are able to tune the symmetry and the magnitude of the magnetic anisotropy.

Spinel structure ferrites constitute a class of materials that has been recognized to have significant technological potential in high-frequency applications. In particular, thin ferrite films exhibit a variety of nonlinear spin-wave phenomena, which are interesting from a fundamental physics perspective as well as from a microwave applications perspective. However, spinel structure ferrite thin films have not lived up to their expectations as extrapolated from their bulk counterparts. Given that they are grown in a nonequilibrium state, it is not surprising that thin ferrite films, be they grown by a layer-by-layer method[1] or by conventional pulsed laser deposition,[2] exhibit some properties very different from bulk ones. Marguiles *et al.*,[3] as well as others,[4,5,6] have found that microstructure plays an important role in the magnetic properties of these ferrite thin films. For example, antiphase boundaries (APB) in spinel structure Fe_3O_4 single-crystal films grown on MgO substrates give rise to anomalous magnetic properties due to an enhanced intrasublattice superexchange coupling. Post deposition annealing has been performed with mixed results.[3,6]

However, APB's can be eliminated by choosing a spinel structure substrate. In this paper, we elucidate the physical origin of anomalous magnetic behavior in spinel structure thin films that are free of APB's in terms of lattice strain and cation disorder. $CoFe_2O_4$ (CFO) is unique among the spinel structure ferrites in that it has a large magnetic anisotropy accompanied by large anisotropic magnetostriction. Therefore effects of strain and cation arrangement, that may have been masked by other effects such as APB's in spinel ferrite thin films grown on MgO substrates, will be enhanced dramatically in the magnetic properties of CFO thin films. While CFO itself is not technologically promising due to its very short spin-lattice relaxation constant, it provides a model system for understanding the magnetic properties of spinel structure ferrite *thin films*. Moreover, the characterization of CFO, thus far, has been based on a few bulk samples of cobalt ferrite accompanied by little theoretical description.[7]

CFO has an inverse spinel structure where the O atoms make up an fcc lattice, an eighth of the tetrahedral (A) sites are occupied by Fe^{3+} ions and half of the octahedral (B) sites are occupied by Co^{2+} and Fe^{3+} ions. The large fraction of empty interstitial sites makes the spinel structure a very open structure conducive to cation migration. Since the Co^{2+} ion is highly anisotropic, it is reasonable that the magnetic behavior of the materials will vary with different Co^{2+} site occupation. Lattice strain effects coupled to spin-orbit coupling and effects of cation migration are expected to be particularly pronounced in CFO where magnetoelastic coupling is strong. In our paper we present a compelling picture of the role of lattice strain and cation migration in epitaxial CFO thin films.

We have grown epitaxial CFO thin films at 400 °C in 7 mTorr O_2 on (110) $MgAl_2O_4$ (MAO) and $CoCr_2O_4$ (CCO) buffered MAO by pulsed laser deposition with thickness of 650 Å to 9000 Å.[8] Microprobe measurements show that the stoichiometry of films is consistent with the target composition to within 2%. Our films exhibit good crystallinity as observed by x-ray diffraction, Rutherford backscattering spectroscopy and transmission electron microscopy (TEM). In the normal incidence $\theta-2\theta$ scans, there is no evidence of the presence of film or buffer orientations other than those of the underlying substrate. The typical full width half maximum rocking curve widths are on the order of 0.4°. In-plane alignment of the crystal axes of the film, buffer, and substrate are indicated by the twofold symmetry of the ϕ scans of the (111) reflections on a (110) oriented sample. Grazing incidence X-ray diffraction (GID) has been used to obtain a direct measure of the strain in our CFO thin films. Table I shows that with the increase of film thickness, the in-plane lattice parameters relax toward bulk value and that a complete relaxation of the strain does not occur even at length scales of 9000 Å. After a post deposition annealing at 1000 °C in air, the compressive strain is further relieved (Table I). The TEM diffraction patterns confirm the excellent epitaxial and crystalline quality of the films. Figure 1 shows a lattice image of a typical (110) oriented CFO film, in cross section, grown under compression. The white line indicates an extra (111) half plane, which forms a Frank dislocation with a burger's vector of $\mathbf{b}=1/3\langle 111\rangle$. The mismatch strains are relieved by forming these edge dislocations. From images of different regions of the specimen, we estimate that

TABLE I. In-plane lattice parameters of CFO films grown on CCO buffered MAO.

Thickness (Å) as-grown	In-plane lattice parameter d_{001}(Å)	In-plane lattice parameter d_{110}(Å)	In-plane strain ε_{001} (%)	In-plane strain ε_{110} (%)
650	8.353±0.006	5.908±0.001	−0.51±0.07	−0.47±0.02
1200	8.359±0.003	5.897±0.003	−0.44±0.04	−0.66±0.05
3600	8.369±0.006	5.899±0.003	−0.32±0.07	−0.62±0.05
9200 after anneal	8.374±0.003	5.908±0.001	−0.26±0.04	−0.47±0.02
650	8.370±0.003	5.910±0.003	−0.31±0.04	−0.44±0.12
1200	8.380±0.010	5.931±0.010	−0.19±0.12	−0.08±0.17
3600	8.389±0.004	5.935±0.010	−0.08±0.05	−0.02±0.17
9200	8.391±0.004	5.947±0.007	−0.06±0.05	+0.17±0.12
Bulk CFO	8.3919	5.9397	/	/

the dislocation density is lower than $1.6\times10^{10}/\text{cm}^2$ in our films.

Given the structural characterization, we expect the lattice strain and relaxation effects to manifest themselves in the magnetic properties of as-grown and annealed CFO films. The magnetic anisotropy of as-grown compressively strained CFO thin films can be understood self consistently from magnetoelastic theory. We have found CFO films grown on (110) $MgAl_2O_4$ (MAO) and $CoCr_2O_4$ buffered (110) MAO to exhibit in-plane uniaxial magnetic anisotropy with an easy [001] and a hard [110] direction.[9] Assuming bulk magnetostriction constants of $\lambda_{100}\sim-590\times10^{-6}$ and $\lambda_{111}\sim120\times10^{-6}$ and elastic constants, $C_{11}=2.73\times10^{12}$ dynes/cm^2, $C_{12}=1.06\times10^{12}$dynes/cm^2 and $C_{44}=0.97\times10^{12}$ dynes/cm^2, we deduce, for the (110) oriented films, the magnetoelastic energy associated with the different in-lane directions to be $E_{me}^{110}=1158\varepsilon\times10^6$ ergs/cm^3, $E_{me}^{111}=1673\varepsilon\times10^6$ ergs/cm^3 and $E_{me}^{001}=2740\varepsilon\times10^6$ ergs/cm^3, where ε is the strain.[10] For films under compression, stress anisotropy makes [001] the magnetically easy and [110] the magnetically hard directions. Since we are comparing the in-plane directions, the demagnetization energy does not play a role here. However there is an additional term due to the crystalline anisotropy energy, which renders the [111] direction the highest-energy state. The observed lowest-energy state is determined by the minimization of the total energy. For films grown on CCO buffered MAO substrates, the mismatch strain is around 0.5% and $K_1\sim1\times10^6$ ergs/cm^3, so that the stress anisotropy term dominates the total energy, thus making [110] the hard direction. For CFO films that we have grown on (100) oriented substrates, similar magnetoelastic arguments can be made.[11] As the magnetocrystalline anisotropy energy is equivalent along the [100], [010], and [001] directions, magnetoelastic energy only competes with the demagnetization energy. The calculation shows that stress anisotropy should dominate and make the in-plane ⟨100⟩ directions to be magnetically easy and hard in films grown under compression and tension, respectively. These calculations are consistent with our observations in Fig. 2.

If indeed the biaxial compressive strain from the lattice mismatch between the film and the substrate is predominant, we should be able to tune such strain anisotropy via the application of external strain. We have performed magnetization measurements on CFO thin films while applying external uniaxial tensile strains along the [110] direction. Figure 3 shows that external strains result in shifts of the anisotropy field from 4.3 T to 1.4 T that in turn allows us to estimate the magnetostriction constants $\lambda_{100}+\lambda_{111}=-120\times10^{-6}$ from

$$\Delta E_{me}=\Delta\int\vec{H}\cdot d\vec{M}=-\frac{3}{4}(\lambda_{100}+\lambda_{111})\cdot A\cdot\int Y\varepsilon_{film}dx,$$

where A is the cross-sectional area and Y is the Young's modulus of the CFO film. These values for magnetostriction

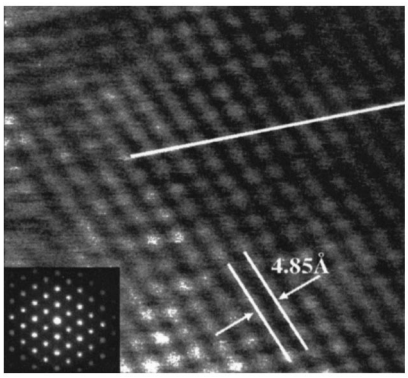

FIG. 1. Lattice image of (110) oriented CFO films on CCO buffered MAO. The white line indicates an extra half ⟨111⟩ plane.

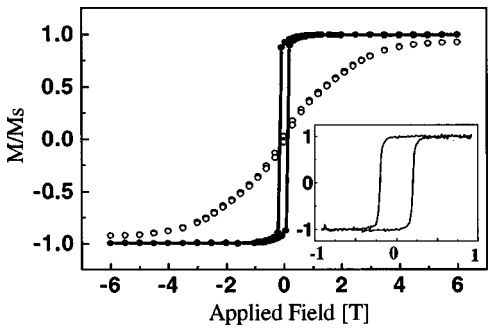

FIG. 2. Magnetization loops of (100) CFO films grown (i) on CCO buffered MAO (solid circles), (ii) on MgO (open circles), with the applied field along in-plane [010] directions. The inset is a detailed plot of (i).

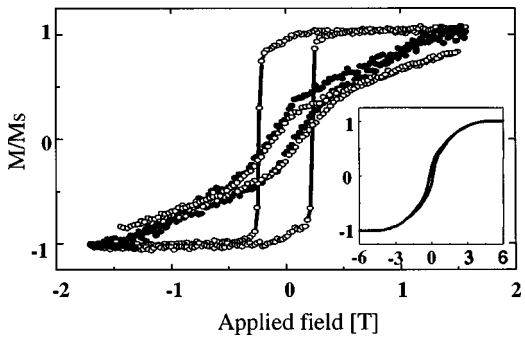

FIG. 3. Magnetization loops of CFO grown on CCO buffered MAO without external stress (open circles) along the easy and hard directions and with external tensile stress along the hard direction (solid circles). External stress shifts the anisotropy field from 4.3 T to 1.4 T. The inset is an expanded plot of the M-H loop along the hard direction without external stress.

confirm the only measure of magnetostriction obtained in single-crystal CFO.[7]

By post deposition annealing that results in strain relaxation (see Table I) and cation redistribution, we varied the magnetoelastic energy contribution to the total energy, as well as the magnetocrystalline energy contribution. We have already explained the twofold symmetry of the (110) oriented as-grown CCO buffered CFO sample in terms of strain due to the lattice mismatch between the film and the substrate [Fig. 4(a)]. When a sample less than 8000 Å thick is annealed at 1000 °C in air for 45 min, we see an inversion of the magnetic anisotropy so that the [001] is the magnetically hard and the [110] is the magnetically easy in-plane direction. From the Co-Fe-O phase diagram, it is extremely unlikely that we are oxidizing any of the Co^{2+} to the Co^{3+} state.[12] Annealing samples in N_2 atmosphere produces the same results, thus suggesting that oxygen content is not the issue. Annealing thicker films (9000 Å) for the same amount of time gives rise to a fourfold symmetry where both [001] and [110] appear to be hard directions [Fig. 4(b)]. However further annealing results in a twofold symmetry of the magnetic anisotropy similar to the thin-film result [Fig. 4(c)]. Since TEM diffraction patterns and normal incidence x-ray measurements did not contain any extra spots or peaks in these annealed films, we believe that there is no phase change during the annealing. Similar experiments of CFO on bare MAO substrates show no anomalous change in the magnetic anisotropy after annealing. Therefore we attribute the fourfold symmetry of the in-plane anisotropy of the thick film to the coexistence of a CFO layer with uniaxial anisotropy plus an interdiffused layer with uniaxial anisotropy of opposite sign. To verify the existence of the interdiffused layer, electron microprobe was used to determine the chromium distribution in an annealed 9000 Å thick film. By varying the acceleration voltage, we were able to adjust the effective range of the electron beam in the film. A peak corresponding to chromium was observed at a depth around 3300 Å, thus suggesting that interdiffusion occurs during the annealing process.

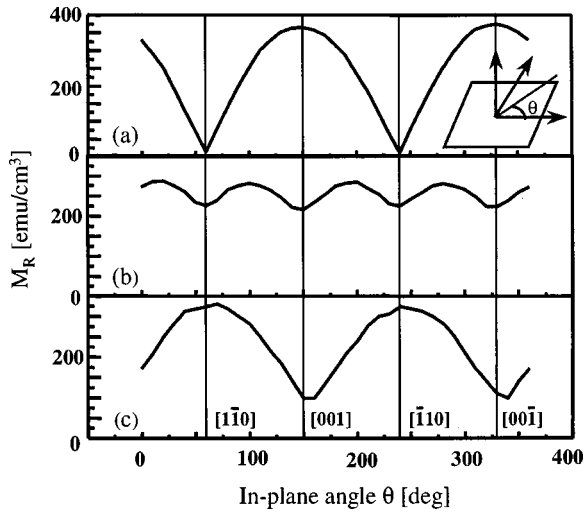

FIG. 4. Remnant magnetization as a function of in-plane angle θ after in-plane saturation for (a) CFO film as-grown (b) CFO film after 45 min annealing (c) CFO film after 3 h annealing.

Comparing the ionic structures of $CoFe_2O_4$ with $CoCr_2O_4$ we assume that the interdiffused layer has a composition of $CoFe_{2-x}Cr_xO_4$. A theoretical calculation of octahedral site preference energy E_B by Paul and Basu[13] shows that Cr^{3+} ions have much larger octahedral affinity than Co^{2+} and Fe^{3+} ions and prefer to stay in the octahedral sites. Indeed bulk studies of the cationic distribution in powder cobalt ferrichromite ($CoFe_{2-x}Cr_xO_4$) show that at small values of x ($\leqslant 0.6$), all of the Cr^{3+} ions exist in octahedral sites, while the same amount of Co^{2+} ions migrate from octahedral to tetrahedral sites to keep half of the octahedral sites occupied.[14] Extended X-ray absorption fine structure (EXAFS) measurements of films on MgO substrates (grown side by side with the buffered MAO substrates during deposition) indicate that $22.57 \pm 2\%$ of the Co^{2+} ions are tetrahedrally coordinated in as-grown films. Considering the nonequilibrium growth of those films, it is reasonable that the as-grown CFO film does not have a completely inverse structure. By post deposition annealing, we observed that the CFO film approached its equilibrium state and to within $\pm 2\%$ all of the Co^{2+} ions were in the octahedral sites. For CFO grown on CCO buffered MAO substrates, due to the buffer layer signal in the EXAFS data, it is difficult to obtain the exact site population of Co^{2+} in CFO films only. However, for thick as-grown films (>5000 Å), where the signal from the CFO layer should dominate, the EXAFS data clearly show a considerable amount of tetrahedrally coordinated Co^{2+} ions. A qualitative comparison of the EXAFS spectra between films before and after annealing indicates that the cobalt site occupation is very similar in these two cases. We believe that the tendency of Cr^{3+} ions to stay in octahedral sites prevents Co^{2+} ions from migrating into the octahedral sites. The distribution of Co^{2+} ions among the two types of sites, in as-grown and annealed samples, determined from EXAFS measurements have also been confirmed by electron energy loss spectroscopy,[11] where a shift of the Co $2P_{3/2}$ peak towards a higher binding energy in annealed film even suggests an increase of the tetrahedrally coordinated Co^{2+} ions.

It is well known that the magnetocrystalline energy in CFO originates from the cations distributed among the tetrahedral and octahedral sites. In garnets, for example, Co^{2+} ions have been shown to give rise to magnetocrystalline

anisotropies of opposite sign depending on its oxygen environment (i.e., Co^{2+} ions in the tetrahedral site have $K_1 \sim -4$ cm^{-1}/ion, while those on octahedral sites have $K_1 \sim +27$ cm^{-1}/ion.[7]). In a study of epitaxial $Y_3Fe_5O_{12}$ (YIG) films, a similar shift of the easy direction, due to post deposition annealing has been reported by Dale *et al.*[15] By comparing the magnetic behavior of cobalt doped YIG films to that of undoped ones, they concluded that the shift resulted from the migration of cobalt ions. Similar results have been obtained by Zhang *et al.*,[16] in their investigation of spinel structure cobalt ferrite.

From the structural evidence, we can confidently state that (i) the large amount of tetrahedrally coordinated Co^{2+} ions and (ii) reduction of the strain are responsible for the evolution of the observed magnetic anisotropy with annealing. After strain relaxation due to post deposition annealing, the magnetocrystalline term now dominates over the strain term in the magnetic anisotropy energy. In order to explain the inversion of magnetic anisotropy and produce an easy axis along the $[\bar{1}10]$ direction, a negative value of K_1 is required. In our case, we believe that the post deposition annealing not only decreases the strain anisotropy energy term in the expression for the total anisotropy energy but also enhances the effect of the negative magnetocrystalline anisotropy K_1 due to Co^{2+} ions on the tetrahedral sites. This results in an overall inversion of the magnetic anisotropy.

In summary, we have explained the origin of the anomalous magnetic behavior in our epitaxial ferrite thin films in terms of cation distribution of Co^{2+} and internal and external lattice strain effects. By varying these parameters, we are able to tune the symmetry and the magnitude of the magnetic anisotropy.

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[1] P. J. van der Zaag, W. F. J. Fontijn, P. Gaspard, R. M. Wolf, V. A. M. Brabers, R. J. M. van de Veerdonk, and P. A. A. van der Heijden, J. Appl. Phys. **79**, 5936 (1996); D. M. Lind, S. D. Berry, G. Chern, H. Mathias, and L. R. Testardi, Phys. Rev. B **45**, 1838 (1992).

[2] P. C. Dorsey, P. Lubitz, D. B. Chrisey, and J. S. Horwitz, J. Appl. Phys. **79**, 6338 (1996); S. B. Ogale, K. Ghosh, R. P. Sharma, R. L. Greene, R. Ramesh, and T. Venkatesan, Phys. Rev. B **57**, 7823 (1998).

[3] D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchson, and A. E. Berkowitz, Phys. Rev. Lett. **79**, 5162 (1997).

[4] F. C. Voogt, T. T. M. Palstra, L. Niesen, O. C. Rogojanu, M. A. James, and T. Hibma, Phys. Rev. B **57**, R8107 (1998).

[5] G. Q. Gong, A. Gupta, Gang Xiao, W. Qian, and V. P. Dravid, Phys. Rev. B **56**, 5096 (1997).

[6] S. Venzke, R. B. van Dover, Julia M. Phillips, E. M. Gyorgy, T. Siegrist, C. H. Chen, D. Werder, R. M. Fleming, R. J. Felder, E. Coleman, and R. Opila, J. Mater. Res. **11**, 1187 (1996).

[7] M. D. Sturge, E. M. Gyorgy, R. C. LeCraw, and J. P. Remeika, Phys. Rev. **180**, 413 (1969).

[8] Y. Suzuki, R. B. van Dover, E. M. Gyorgy, Julia M. Phillips, V. Korenivski, D. Werder, C. H. Chen, R. J. Cava, J. J. Krajewski, W. F. Peck, and K. B. Do, Appl. Phys. Lett. **68**, 714 (1996).

[9] Y. Suzuki, G. Hu, R. J. Cava, and R. B. van Dover, J. Magn. Magn. Mater. **105**, 1 (1999).

[10] See, for example, R. M. Bozorth, *Ferromagnetism* (D. van Nostrand Company, Inc., New York, NY, 1951), p. 582.

[11] G. Hu, T. K. Nath, C. B. Eom, and Y. Suzuki (unpublished).

[12] M. Takahashi and M. E. Fine, J. Am. Ceram. Soc. **54**, 291 (1971).

[13] A. Paul and S. Basu, Trans. Br. Ceram. Soc. **73**, 167 (1974).

[14] A. Hauet, J. Teillet, B. Hannoyer, and M. Lenglet, Phys. Status Solidi A **108**, 257 (1987).

[15] Darren Dale, G. Hu, Vincent Balbarin, and Y. Suzuki, Appl. Phys. Lett. **74**, 3026 (1999).

[16] H. Y. Zhang, B. X. Gu, H. R. Zhai, M. Lu, Y. Z. Miao, S. Y. Zhang, and H. B. Huang, J. Appl. Phys. **75**, 7099 (1994).