

Cation-disorder-enhanced magnetization in pulsed-laser-deposited CuFe_2O_4 films

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Copper ferrite films have been deposited on (100) MgO substrates by pulsed-laser deposition. The oxygen pressure used in deposition was varied from 1 to 120 mTorr with the substrate temperature fixed at 700 °C. Magnetization values are measured to increase with oxygen pressure, reaching a maximum value of 2480 G, which is a 42% increase over the bulk equilibrium value. Extended x-ray absorption spectroscopy shows that the Cu cation inversion δ [defined as $(\text{Cu}_{1-\delta}\text{Fe}_\delta)^{\text{tet}}[\text{Cu}_\delta\text{Fe}_{2-\delta}]^{\text{oct}}\text{O}_4$] decreases monotonically from 0.72 to 0.55 with increasing saturation magnetization. © 2005 American Institute of Physics. [DOI: 10.1063/1.1952571]

In the spinel ferrite structure, oxygen atoms form a close packed lattice with transition metal cations residing at the interstices. Specifically, 8 of 64 tetrahedrally coordinated (A) sites and 16 of the 32 octahedrally coordinated (B) sites are filled by magnetic, and often nonmagnetic, cations. The type, valence, and distribution of these cations influence to a large degree the material's magnetic and electronic properties. Copper ferrite in its bulk form is a mixed spinel, with approximately 85% of the Cu ions occupying the octahedral sublattice, with Fe cations filling the remainder of the sites.¹ The structure is described by the formula $(\text{Cu}_{1-\delta}\text{Fe}_\delta)^{\text{tet}}[\text{Cu}_\delta\text{Fe}_{2-\delta}]^{\text{oct}}\text{O}_4$, where δ is the inversion coefficient (0.85). Density functional theory calculations suggest that if the cation distribution can be varied, that is, increasing the Cu^{2+} on the tetrahedral sublattice, the imbalance in sublattice spins will result in an increase in the room temperature magnetization. Hence, control of the cation distribution may allow for enhancement of the magnetic properties, namely, magnetization and anisotropy, valuable for microwave applications.

In this letter, we report the magnetic, microstructure, and local atomic structural properties of pulsed-laser-deposited Cu ferrite films on (100) MgO. By applying extended x-ray absorption fine structure (EXAFS) spectroscopy²⁻⁴ to a series of films deposited under different oxygen pressures, the cation distribution is determined and correlated with the magnetic properties. A maximum value of saturation magnetization, 2480 G, was measured for high-pressure deposition and is 42% higher than the bulk equilibrium value. EXAFS-determined Cu cation inversion δ decreases monotonically from 0.72 to 0.55 with increasing saturation magnetization.

Copper ferrite thin films were deposited by 8000 laser pulses at 400 mJ incident energy upon a CuFe_2O_4 target. The films were deposited on single-crystal (100) MgO substrates; MgO was chosen for its close lattice match with Cu ferrite. MgO preserves the cubic structure with lattice parameter 4.216 Å [while the lattice parameter of Cu ferrite is 8.445 Å (see Ref. 5)], nearly twice that of MgO substrate, resulting in a lattice mismatch of $\sim 0.15\%$. The thermal expansion coefficient of spinel ferrites range from 7.5×10^{-6} to $12 \times 10^{-6} \text{ K}^{-1}$,⁶ which is comparable to the MgO value of $12.8 \times 10^{-6} \text{ K}^{-1}$.⁷ Hence, we can expect little strain in the growing film. Film thicknesses are measured to be of the order of 1000 Å. At a fixed temperature of 700 °C, a series of films was grown at oxygen pressures ranging from 1 to 120 mTorr. All the samples were characterized using vibrating sample magnetometer, ferromagnetic resonance, atomic force microscopy (AFM), soft X-ray absorption spectroscopy (XAS), and EXAFS.⁸ EXAFS analysis of cation distribution was first performed by Harris *et al.* in 1996.³ This approach has been extended by Calvin *et al.*, who, in 2002, performed the first multiedge refinement of the spinel structure.² Both Harris *et al.* and Calvin *et al.* made use of theoretical standards generated by FEFF codes of Rehr *et al.*⁹ together with the well established EXAFS refinement procedures outlined by Sayers and Bunker in Ref. 4. Here, we report a similar multi-edge refinement of spinel ferrite using the ATHENA and ARTEMIS codes of Ravel *et al.*¹⁰ and Newville,¹¹ respectively, to analyze the cation distribution of samples produced under different pulsed-laser deposition (PLD) oxygen pressures.

Cu ferrite films reported here have well-defined in-plane uniaxial anisotropy fields (H_a). Values range from 450–550 Oe for samples having a large cation disorder (processed using moderate to high oxygen pressures). The aniso-

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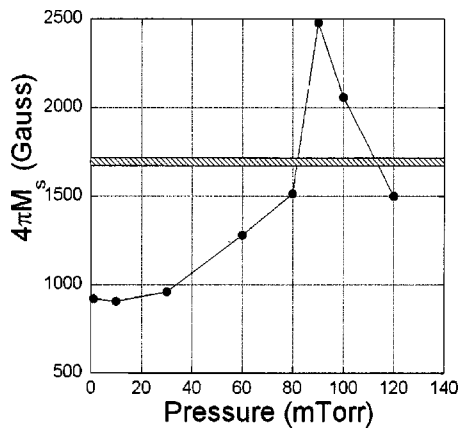


FIG. 1. Variation of saturation magnetization of copper ferrite thin films as a function of oxygen pressure used in pulsed-laser deposition.

ropy field is measured to track the cation disorder with the highest values corresponding to the lowest oxygen pressures and the highest δ values. These samples also have x-ray diffraction (XRD) peaks that are indexed to the tetragonal spinel phase.¹² The source of the magnetic anisotropy is attributed to the magnetocrystalline anisotropy mechanism.¹³ The coercivity is nearly constant for all samples at ~ 200 Oe. AFM images of films show large cubic crystals, 500 nm on a side, with an average surface roughness of >5 nm at low deposition pressures (i.e., 1 mTorr) and smooth featureless surfaces at high deposition pressures (<1 nm average surface roughness).¹⁴

Figure 1 shows the variation of saturation magnetization as a function of oxygen pressure used in PLD. There appears a clear trend of increasing magnetization with increasing oxygen deposition pressure up to 90 mTorr, with a sharp decrease at higher pressure values. We obtained the highest value of $4\pi M_s$ —2481 G—for the sample deposited at 90 mTorr. In this figure, the magnetization of the bulk material is plotted as a reference. Compared with the bulk, the sample grown at 90 mTorr has a 42% larger magnetization. The bulk room temperature magnetization of the spinel copper ferrite is 1700 G.¹⁵

The samples prepared at 1, 60, 80, 90, 100, and 120 mTorr were all prepared for EXAFS analysis. The real part of Fourier transform amplitude of the EXAFS data and the best fits are shown in Fig. 2. As seen in Fig. 2, the EXAFS model created for the spinel ferrite closely matches the experimental data for all samples. The R factors for the best fit to the experimental data are consistently below 0.05, generally considered a good fit for EXAFS modeling of spinel structures.² The EXAFS-determined inversion coeffi-

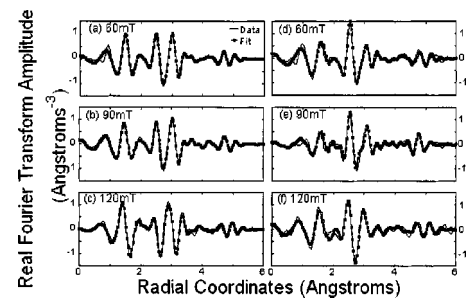


FIG. 2. Real part of the Fourier transform amplitude of EXAFS data with best fits. Panels (a), (b), and (c) are for Fe K -edge absorption while panels (d), (e), and (f) are for the Cu K -edge absorption. Deposition pressures are denoted on each panel.

icients and other relevant parameters are listed in Table I. The subtle differences that exist between best fit and experimental data arise from the constraints used in the spinel model.⁵ From this analysis, we can conclude that the lattice parameters are reduced compared with the bulk value of 8.445 Å.⁵ Additionally, it is calculated that the δ changes from 0.55 to 0.72. Figure 3 shows the variation of $4\pi M_s$ as a function of the δ . The saturation magnetization shows a monotonic increase with decreasing inversion parameter. These findings agree with the density functional theory prediction that an increase in the fraction of Cu^{2+} ($\mu_B=1$) on the tetrahedral sublattice, and the corresponding increase of Fe^{3+} ($\mu_B=5$) on the octahedral sublattice, increases the net magnetization of the structure due to the magnetic imbalance between these ferrimagnetic coupled sublattices.

The saturation magnetization changes as a function of pressure and with the changing δ . As is seen in Fig. 3, the samples grown at lower pressures have a reduced magnetization compared with the bulk value. We speculate that the reduction of the magnetization at low pressures is due to the incomplete oxidation of the cations, resulting in anion defects in the film. The anion defects have a direct role in magnetization since the superexchange mechanism relies upon anion mediation of cation electron wave functions. This interpretation is supported by high precision, $L_{2,3}$ -edge XAS of Cu and Fe. It has been reported that white lines of L_3 edges of ferrite materials shift to higher energies, while the oxidation state changes from +2 to 0.^{16,17} The energy of the L_3 edge in the sample processed at 90 mTorr is 929.1 eV, and the multiplets of the L_3 edge in 1 mTorr sample are 929.4 and 932.5 eV. Although we cannot quantify the exact valence of Cu, it can be concluded that the samples processed at lower pressures are oxidized to a valence less than +2.

TABLE I. Results of fitting EXAFS data to a theoretical standard. Uncertainties in the least significant digit are given in parentheses.

	60 mTorr	80 mTorr	90 mTorr	100 mTorr	120 mTorr	Bulk ^a
Lattice parameter (Å)	8.376(2)	8.332(3)	8.369(2)	8.343(2)	8.417(2)	8.445
Oxygen parameter	0.390(1)	0.391(1)	0.392(1)	0.393(6)	0.390(1)	0.38
Octahedral (%)						
copper	70.9(2.0)	71.6(2.3)	54.0(6.4)	54.4(4.7)	67.7(2.5)	85
Iron (calculated)	64.6	64.3	72.9	72.8	66.7	57.5
R factor	0.03	0.03	0.05	0.03	0.04	...

^aSee Refs. 1, 15, and 16.

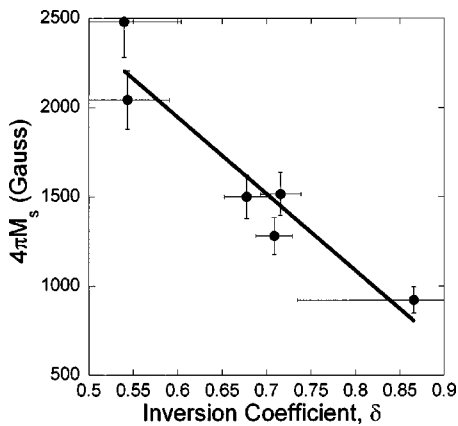


FIG. 3. Variation of saturation magnetization as a function of inversion coefficient δ .

At higher pressures, the frequency of ablated ion collisions within the oxygen plasma is increased, resulting in the complete oxidation of the cations during film growth. However, the increase in collisions also results in the loss of ion kinetic energy and a subsequent reduction in adatom mobility. This decrease in surface mobility leads to an increase in the cation disorder, as evidenced by the decrease in δ .

To further study the relationship between structure, disorder, and magnetization, the 90 mTorr sample was annealed at 800 °C for 2 h and slow-cooled in air. The saturation magnetization was found to be reduced from 2450 to 1900 G, 12% higher than the bulk value. Its XRD pattern showed some peaks that were indexed to the tetragonal spinel phase. Additionally, the sample was annealed again to 800 °C for 2 h after which it was quenched in air. As expected, the $4\pi M_s$ returned to 2480 G. This behavior, as seen in Fig. 4, confirms that not only the crystal structure and cation disorder relate to thermal treatment, but the cation distribution also plays a large role in determining the saturation magnetization. It is noteworthy that bulk Cu ferrite samples quenched under similar conditions also experience increased cation disorder.¹⁸ However, the degree of disorder is less than that measured in film samples. We speculate that lattice strain from both a mismatch in lattice parameter and thermal expansion coefficient between the film and substrate may be responsible for enhancing this affect.

In summary, this letter describes studies performed on Cu ferrite films in which the Cu cation inversion coefficient is systematically reduced compared with the bulk value of 0.85 to ~ 0.55 . As a result of this reduction, the room temperature saturation magnetization is increased as much as 42%. Annealing studies confirm that the cation disorder is related to the effective quench rate used in processing and to the magnetization values. These studies demonstrate the ability to control and enhance magnetic properties relative to equilibrium values. This approach provides new opportunities for the design and processing of nonequilibrium spinel ferrites, which may provide solutions to microwave magnetic integrated circuit applications.

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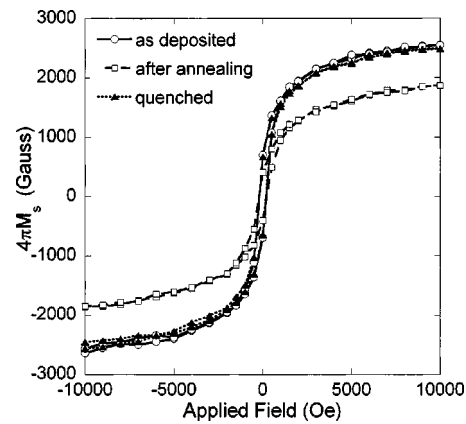


FIG. 4. Hysteresis loops (as $4\pi M_s$ vs H_{app}) of CuFe_2O_4 films in the as-deposited 90 mTorr, annealed-slow cooled, and annealed-quenched states.

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¹F. Bertaut, *Compt. Rend.* **230**, 213 (1950).

²S. Calvin, E. E. Carpenter, V. G. Harris, and S. Morrison, *Appl. Phys. Lett.* **81**, 3828 (2002).

³V. G. Harris, N. C. Koon, C. M. Williams, Q. Zhang, M. Abe, and J. P. Kirkland, *Appl. Phys. Lett.* **68**, 2082 (1996).

⁴D. E. Sayers and B. A. Bunker, *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES* (Wiley, New York, 1988), Vol. 92, p. 211.

⁵R. W. G. Wyckoff, *Crystal Structure* (Interscience, New York, 1965), p. 79.

⁶E. P. Wohlfarth, *Ferromagnetic Materials: A Handbook on the Properties of Magnetically Ordered Substances* (North-Holland, Dordrecht, 1982), p. 289.

⁷Thermal expansion coefficient of MgO value is provided by MTI Corporation.

⁸X-ray absorption spectra were collected at the National Synchrotron Light Source using the beamlines X23B and U4B. Data collection was performed in fluorescence yield at room temperature under standard conditions. At the time data were collected the storage ring energy was 2.54 GeV and the ring current ranged from 180 to 250 mA.

⁹J. J. Rehr, S. I. Zabinsky, and R. C. Albers, *Phys. Rev. Lett.* **81**, 3828 (2002).

¹⁰B. Ravel and M. Newville, *Proceedings of the 12th Annual XAFS Conferences [Physica Scripta]*, T115, 1007 (2005).

¹¹M. Newville, *J. Synchrotron Radiat.* **8**, 322 (2001).

¹²E. Prince and R. G. Treuting, *Acta Crystallogr.* **9**, 1025 (1956). It is reported that Cu-ferrite experiences a tetragonal distortion when quenched from below 760 °C. Quenching from above (760 °C), copper ferrite will maintain its cubic spinel structure. All of the samples presented here were quenched from the vapor phase onto a 700 °C substrate and then further quenched in an oxygen atmosphere to room temperature. The XRD peaks of the sample prepared at 90 mTorr can be indexed to the cubic spinel structure, while samples processed at lower pressures have diffraction peaks indexed to both cubic and tetragonal spinel phases.

¹³S. Chikazumi, *Physics of Ferromagnetism*, Oxford Science Publications (Oxford University Press, Oxford, 1997), p. 249.

¹⁴A. Yang, X. Zuo, L. Chen, Z. Chen, C. Carmine, and V. G. Harris, *J. Appl. Phys.* **97**, 10G107 (2005).

¹⁵J. Smit and H. P. J. Wijn, *Ferrites* (Wiley, New York, 1959), p. 157.

¹⁶R. D. Leapman, L. A. Grunes, and P. L. Fejes, *Phys. Rev. B* **26**, 614 (1982).

¹⁷S. L. Hulbert, B. A. Bunker, and F. C. Brown, *Phys. Rev. B* **30**, 2120 (1984).

¹⁸*Crystal and Solid State Physics*, edited by K.-H. Hellwege and A. M. Hellwege, Landoldt-Börnstein, New Series, Group III, Vol. 4, Pt. B (Springer, Berlin, 1970), p. 345, and references contained therein.