

Temperature dependence of magnetic anisotropy in Mn-substituted cobalt ferrite

Y. Melikhov, J. E. Snyder, and D. C. Jiles

Materials Science and Engineering Department, Iowa State University, Ames, Iowa 50011

A. P. Ring, J. A. Paulsen, and C. C. H. Lo

Center for Nondestructive Evaluation, Iowa State University, Ames, Iowa 50011

K. W. Dennis

Materials and Engineering Physics Program, Ames Laboratory, U.S. Department of Energy, Ames, Iowa 50011

(Presented on 3 November 2005; published online 18 April 2006)

The temperature variation of magnetic anisotropy and coercive field of magnetoelastic manganese-substituted cobalt ferrites ($\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ with $0 \leq x \leq 0.6$) was investigated. Major magnetic hysteresis loops were measured for each sample at temperatures over the range 10–400 K, using a superconducting quantum interference device magnetometer. The high-field regimes of the hysteresis loops were modeled using the law of approach to saturation equation, based on the assumption that at sufficiently high field only rotational processes remain, with an additional forced magnetization term that was linear with applied field. The cubic anisotropy constant K_1 was calculated from the fitting of the data to the theoretical equation. It was found that anisotropy increases substantially with decreasing temperature from 400 to 150 K, and decreases with increasing Mn content. Below 150 K, it appears that even under a maximum applied field of 5 T, the anisotropy of CoFe_2O_4 and $\text{CoMn}_{0.2}\text{Fe}_{1.8}\text{O}_4$ is so high as to prevent complete approach to saturation, thereby making the use of the law of approach questionable in these cases. © 2006 American Institute of Physics. [DOI: [10.1063/1.2151793](https://doi.org/10.1063/1.2151793)]

INTRODUCTION

Magnetoelastic materials exhibit changes in their magnetization in response to applied stress or torque. These changes may be sensed remotely by measuring changes in external magnetic field (“fringing” field), and this phenomenon can be used for stress and torque sensor applications. Cobalt ferrite and metal-bonded cobalt ferrite composites¹ and their Mn-substituted modifications² show promising magnetomechanical properties for use in such sensors because of their high levels of magnetostriction λ and its derivative $d\lambda/dH$, which can be selected by control of the Mn content. Substituting Mn for Fe in cobalt ferrite allows adjustment of the Curie temperature of the material,² thereby influencing the temperature dependence of its stress sensitivity and magnetomechanical hysteresis.

However, there is much that is still not understood about the magnetomechanical properties of these materials. In particular, further investigation is required of the temperature dependence of the magnetomechanical response, which is strongly dependent on the magnetostriction and magnetic anisotropy, as well as magnetic coercivity, permeability, and chemical composition of the material. In the present study we report the results of a systematic study of the effect of substitution of Mn for Fe in CoFe_2O_4 on magnetic anisotropy and coercive field at different temperatures, from 10 to 400 K, for a series of sintered bulk Mn-substituted cobalt ferrites of composition $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ for $0 \leq x \leq 0.6$.

EXPERIMENTAL DETAILS AND RESULTS

A series of manganese-substituted cobalt ferrite samples with general compositions $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ (where x ranges from 0 to 0.6) was prepared by standard powder ceramic techniques² with a final sintering at 1350 °C for 24 h and subsequent furnace cooling to room temperature. The actual compositions, which were determined using energy dispersive x-ray spectroscopy in a scanning electron microscope (SEM), were found to be close to the target compositions. X-ray powder diffractometry study showed a single-phase cubic spinel crystal structure for all samples. SEM studies showed a dense, homogeneous microstructure of equiaxed grains of typically 10 μm in diameter in all samples.

Vibrating sample magnetometer measurements were conducted to determine the Curie temperature T_C of the samples, which was found to decrease linearly from 784 K for pure cobalt ferrite to 577 K for $\text{CoMn}_{0.6}\text{Fe}_{1.4}\text{O}_4$.² Using a superconducting quantum interference device (SQUID) magnetometer, the temperature dependence of magnetization under an applied field of 5 T (50 kOe) was recorded, on cooling from 400 to 10 K (Fig. 1). Although an apparent decrease in magnetization was observed for the CoFe_2O_4 and $\text{CoMn}_{0.2}\text{Fe}_{1.8}\text{O}_4$ samples for temperatures below about 160 and 130 K, respectively, this appeared to be due to the applied field no longer being able to saturate these samples at these temperatures (see the Discussion section below). Measurements of major hysteresis loops were also made at selected temperatures over the range 10–400 K using the SQUID magnetometer. The maximum applied magnetic field

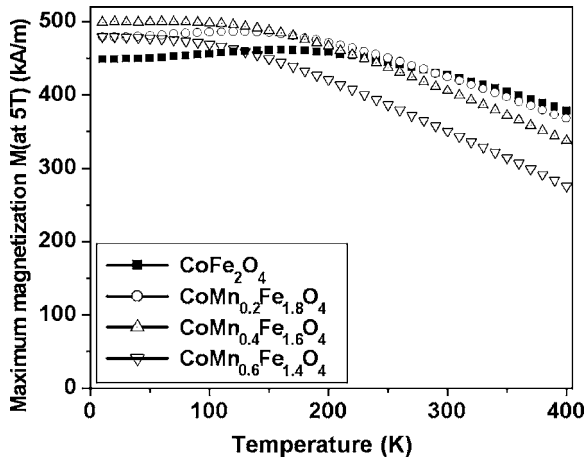


FIG. 1. Temperature dependence of maximum magnetization for Mn-substituted cobalt ferrites, measured under a constant magnetic field of 5 T.

was 5 T. As an example, the first quadrant portion of major hysteresis loops for $\text{CoMn}_{0.4}\text{Fe}_{1.6}\text{O}_4$ at different temperatures is shown in Fig. 2. The coercive field H_C for different compositions and different temperatures is shown in Fig. 3.

In order to evaluate the temperature dependence of the anisotropy, it was assumed that all irreversible hysteretic processes were completed when the major hysteresis loop closed and that further increase of the magnetic moment was due to rotational processes which are connected with the magnetic anisotropy. Based on the law of approach (LA) to saturation, which describes the dependence of magnetization M on the applied field for $H \gg H_C$, magnetization near the saturation magnetization M_S can be approximated by³

$$M = M_S \left[1 - \frac{8}{105 \mu_0^2 M_S^2} \left(\frac{K_1}{H} \right)^2 \right] + \kappa H, \quad (1)$$

where the numerical coefficient 8/105 is for random polycrystalline specimens with cubic anisotropy, and K_1 is the cubic anisotropy constant (the one-constant approximation to cubic anisotropy is assumed). The term κH describes forced magnetization due to an increase of the spontaneous magne-

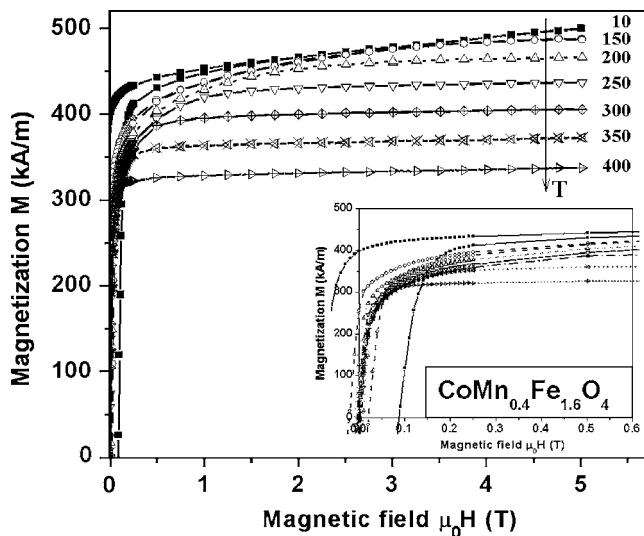


FIG. 2. Major hysteresis loops of $\text{CoMn}_{0.4}\text{Fe}_{1.6}\text{O}_4$ for different temperatures.

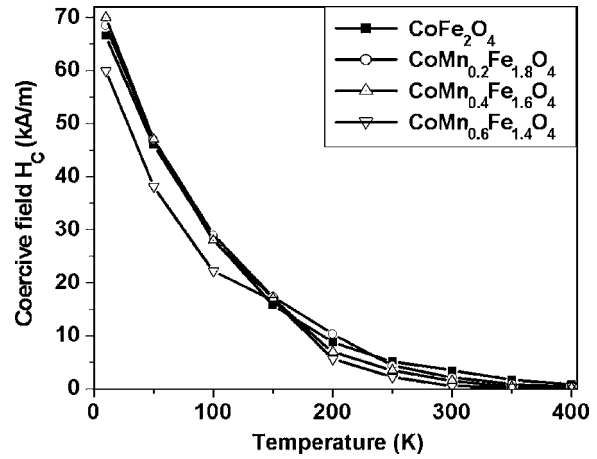


FIG. 3. Coercive field as a function of temperature for manganese-substituted cobalt ferrite samples $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ with various manganese contents ($x=0$ to 0.6).

tization in high fields, where the parameter κ is the high-field susceptibility. The forced magnetization term was found to be necessary to fit the hysteresis curves at higher temperatures and higher fields.

The high-field parts of the major hysteresis curves were fitted using the standard LA approach by Eq. (1). For temperatures above 150 K, using only the parts of the curves with fields higher than 1 T, the best values of M_S , K_1 , and κ to describe the data were calculated. For temperatures below 150 K, only the parts of the curves with fields higher than 2.5 T were compared with Eq. (1). Detailed examination of the curves revealed that forced magnetization was negligible in this regime, as might be expected. Therefore, $\kappa=0$ and consequently M_S and K_1 were the only fitting parameters. The temperature dependence of the calculated anisotropy K_1 for different manganese contents is shown in Fig. 4. The values of saturation magnetization M_S computed by fitting Eq. (1) to experimental data were found to be approximately the same as the measured maximum magnetization (K) values at 5 T, ex-

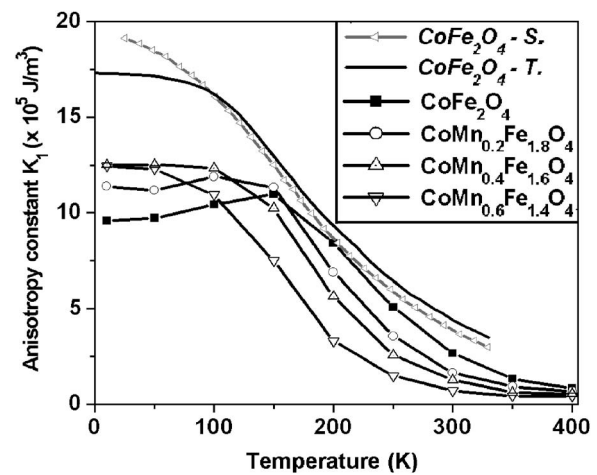


FIG. 4. Cubic anisotropy constant, K_1 , determined by law of approach to saturation, vs temperature for manganese-substituted cobalt ferrite samples $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ with various manganese contents ($x=0$ to 0.6). Experimental data (Ref. 7) for single-crystal pure cobalt ferrite (marked as $\text{CoFe}_2\text{O}_4\text{-S}$) and theoretical calculations (Ref. 8) for pure cobalt ferrite (marked as $\text{CoFe}_2\text{O}_4\text{-T}$) are presented for comparison.

cept for temperatures above 150 K, where the maximum magnetization measured is larger than M_S by several percent due to the occurrence of forced magnetization.

DISCUSSION

The analysis of temperature dependence of the anisotropy constant K_1 for $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ can be divided into two regions: above and below 150 K (see Fig. 4). For temperatures above 150 K, the anisotropy of all the Mn-substituted cobalt ferrites increases substantially with decreasing temperature, to values that are of the order of magnitude 10^6 J/m^3 (or 10^7 erg/cm^3). Also, at each specific temperature anisotropy decreases with increasing Mn content. However, below 150 K dependence of the calculated anisotropy on temperature becomes more complicated: as temperature decreases, K_1 continues to increase for the specimen with $x=0.6$, however, at a slower rate; it appears to level off at the lowest two temperatures for the specimen with $x=0.4$; and it appears to decrease for the sample with $x=0.2$ and pure cobalt ferrite ($x=0.0$). These anomalous decreases are most likely due to the applied field strength no longer being able to saturate the sample since anisotropy is increasing to very high levels.

The dependence of maximum magnetization on temperature (Fig. 1) also supports the conclusion that 5 T is not enough to saturate the specimens at low temperatures (below about 150 K), especially for pure cobalt ferrite or specimens with lower manganese content. For example, for $x=0$ and $x=0.2$ magnetization reaches a maximum at temperatures ~ 150 K and then slightly decreases, which suggests that the anisotropy has become so high that the samples could not be magnetized sufficiently close to saturation for the fitting method to be able to extract an accurate value for K_1 . Indeed, for the pure cobalt ferrite, the anisotropy field⁴ $H_K = 2K_1/\mu_0 M_S$ was estimated to be 4.7 T at 150 K. It would therefore be expected that, as the anisotropy further increases for temperatures below 150 K, 5 T would not be enough to magnetize the sample to saturation.

Only the absolute value of the cubic anisotropy constant K_1 can be extracted from the LA composition approach [see Eq. (1)]. To second order, the numerical expression is the same for the [100] and [111] easy axes. However, it has been reported in the literature that the anisotropy of cobalt ferrite is positive, i.e., $\langle 100 \rangle$ are the easy axes⁵ and the reported values for 300 K range from $2.1 \times 10^5 \text{ J/m}^3$ to $3.9 \times 10^5 \text{ J/m}^3$ depending on the stoichiometry of the material and heat treatment.^{6,7} In the present study, the magnitude of the anisotropy of pure CoFe_2O_4 was found to be $2.7 \times 10^5 \text{ J/m}^3$ ($2.65 \times 10^6 \text{ erg/cm}^3$) at 300 K, which is consistent with values reported in the literature. Moreover, for temperatures above 150 K our method for determination of the anisotropy constant K_1 for these ferrites is supported by the experimental data for pure cobalt ferrite of Shenker,⁷ who measured anisotropy of single-crystal cobalt ferrite by a modified torque magnetometer method, and by the theoretical work of Tachiki⁸ (see Fig. 4).

The observed decrease in anisotropy of cobalt ferrite with manganese content can be interpreted in terms of the

effects of Mn substitution on site occupancies of the cations. According to the one-ion model, the strong anisotropy of cobalt ferrite is primarily due to the presence of Co^{2+} ions on the octahedral sites of the spinel structure.⁹ The results of our recent Mössbauer spectroscopy studies of the Mn-substituted cobalt ferrites suggest that, in substituting manganese for iron, Mn^{3+} goes into the octahedral sites, and at least some of the Co^{2+} ions are displaced from octahedral to tetrahedral sites.¹⁰ This supports the observed decrease in anisotropy with increasing Mn content, found for all temperatures in the temperature region above 150 K where a good agreement with the law of approach equation could be obtained.

CONCLUSIONS

The temperature dependence of magnetic anisotropy of polycrystalline manganese-substituted cobalt ferrite specimens of composition $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ with $0 \leq x \leq 0.6$ was investigated. Magnetic anisotropy constants were obtained from fitting of the high-field parts of the major hysteresis loops with the LA equation, with an additional term to express the forced magnetization contribution. It was found that between 400 and 150 K, the anisotropy of all Mn-substituted cobalt ferrites increases substantially with decreasing temperature and decreases with increasing Mn content. The decrease with increasing Mn content is consistent with our interpretation of recent Mössbauer spectroscopy measurements, taking into account the one-ion anisotropy model. It was also concluded that below 150 K the anisotropy is so high that the applied magnetic field of 5 T does not magnetize the specimens sufficiently close to saturation to enable extraction of an accurate value for K_1 by the LA method. This accounts for the apparent decrease in the calculated anisotropy as temperature decreases below 150 K for the pure cobalt ferrite and low Mn content samples.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation, Division of Materials Research, under Grant No. DMR-0402716 and the National Aeronautical and Space Administration (NASA) under Award No. NAG-1-02098. This work was also supported in part by the U.S. DOE, office of Basic Energy Science, Materials Science Division. Ames Laboratory is operated for the U.S. DOE by ISU under Contract Number W-7405-ENG-82.

¹R. W. McCallum, K. W. Dennis, D. C. Jiles, J. E. Snyder, and Y. H. Chen, *Low Temp. Phys.* **27**, 266 (2001).

²J. A. Paulsen, A. P. Ring, C. C. H. Lo, J. E. Snyder, and D. C. Jiles, *J. Appl. Phys.* **97**, 044502 (2005).

³S. Chikazumi, *Physics of Ferromagnetism*, 2nd ed. (Oxford University Press, Oxford, 1997), pp.503–508.

⁴B. D. Cullity, *Introduction to Magnetic Materials* (Addison-Wesley, Reading, MA, 1972), p.233.

⁵J. Smit, *Ferrites* (Wiley, New York, 1959), p.163.

⁶R. M. Bozorth, E. F. Tilden, and A. J. Williams, *Phys. Rev.* **99**, 1788 (1955).

⁷H. Shenker, *Phys. Rev.* **107**, 1246 (1957).

⁸M. Tachiki, *Prog. Theor. Phys.* **23**, 1055 (1960).

⁹J. C. Slonczewski, *Phys. Rev.* **110**, 1341 (1958).

¹⁰K. Kriebel, T. Schaeffer, J. A. Paulsen, A. P. Ring, C. C. H. Lo, and J. E. Snyder, *J. Appl. Phys.* **97**, 10F101 (2005).