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Temperature dependence of magnetic anisotropy of germanium/cobalt cosubstituted cobalt ferrite

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The variations in magnetization and magnetic anisotropy of $\text{Ge}^{4+}/\text{Co}^{2+}$ cosubstituted cobalt ferrite with temperature were investigated for a series of compositions $\text{Co}_{1+x}\text{Ge}_x\text{Fe}_{2-2x}\text{O}_4$ ($0 \leq x \leq 0.4$). The magnetization at 5 T and low temperature were observed to increase for all Ge/Co cosubstituted samples compared to pure CoFe_2O_4 . Hysteresis loops were measured for each sample over the magnetic field range of -5 T to $+5$ T for temperatures in the range of 10–400 K. The high field regions of these loops were modeled using Law of Approach to saturation, which represents the rotational and forced magnetization processes. The first order cubic magnetocrystalline anisotropy coefficient K_1 was calculated from these fits. K_1 decreased with increasing Ge content at all temperatures. Anisotropy increased substantially as temperature decreased. Below 150 K, for certain compositions ($x=0, 0.1, 0.2$, and 0.3), the maximum applied field of $\mu_0 H=5$ T was less than the anisotropy field and therefore insufficient to saturate the magnetization. In these cases, the use of the Law of Approach model can give values of K_1 that are lower than the correct values and this method cannot be used to estimate anisotropy accurately under these conditions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3077201]

I. INTRODUCTION

There has been a recent interest in cobalt ferrite based materials because of their high magnetostrictive strain amplitude, high magnetostrictive strain derivative (rate of change in magnetostrictive strain with applied field), and low hysteresis, which makes them a candidate material for high performance stress/torque sensor and actuator applications.^{1–6} Chemical substitution can enhance the properties of cobalt ferrite by altering the cation distribution in the cubic spinel structure, therefore, influencing the magnetoelastic properties of these materials. Previous studies have shown that the substitution of M^{3+} (Mn^{3+} , Cr^{3+} , and Ga^{3+})^{2,3,7} in place of some of Fe^{3+} reduces the hysteresis and increases the strain derivative of cobalt ferrite for certain compositions with, however, a decline or no improvement in the magnitude of magnetostrictive strain amplitude. The change in magnetoelastic properties of these materials can be explained in terms of the change in important magnetic properties such as the magnetization characteristics and magnetocrystalline anisotropy.

In the present study, we have investigated a new cosubstitution of $\text{Ge}^{4+}/\text{Co}^{2+}$ in place of some of Fe^{3+} in cobalt ferrite. The high tetrahedral site preference of Ge^{4+} in the cubic spinel lattice of cobalt ferrite and the additional substitution of Co^{2+} produced a more favorable change in properties in comparison to previously tried substitutions.

II. EXPERIMENT AND RESULTS

A series of randomly oriented polycrystalline $\text{Ge}^{4+}/\text{Co}^{2+}$ cosubstituted cobalt ferrite samples with general composition

of $\text{Co}_{1+x}\text{Ge}_x\text{Fe}_{2-2x}\text{O}_4$ was made by standard powder ceramic techniques with a final sintering at 1350 °C for 24 h, followed by furnace cooling to room temperature.^{1,3} The target compositions had a germanium content of $x=0, 0.1, 0.2, 0.3$, and 0.4 . The actual compositions were determined using energy dispersive x-ray spectroscopy (EDS) in a scanning electron microscope (SEM) and were found to be close to the target compositions, as shown in Table I. The Curie temperatures of Ge/Co cosubstituted cobalt ferrite have been found to decrease with increasing x .⁸

The variation in technical saturation of magnetization with temperature was measured using a superconducting quantum interference device (SQUID) magnetometer at an applied field of $\mu_0 H=5$ T. As can be seen in Fig. 1, the magnetization increased monotonically with decreasing temperature over the range of 400–160 K for all samples. The apparent saturation magnetization decreased for CoFe_2O_4 below 160 K, for $\text{Co}_{1.1}\text{Ge}_{0.1}\text{Fe}_{1.8}\text{O}_4$ below 128 K, and for $\text{Co}_{1.2}\text{Ge}_{0.2}\text{Fe}_{1.6}\text{O}_4$ below 78 K. For all other samples, saturation magnetization was observed to increase with decreasing temperature throughout the entire temperature range.

TABLE I. Comparison of target and actual compositions in $\text{CoGe}_x\text{Fe}_{2-2x}\text{O}_4$.

Target compositions	Composition by EDS		
	Fe	Co	Ge
CoFe_2O_4	2.05	0.95	...
$\text{Co}_{1.1}\text{Ge}_{0.1}\text{Fe}_{1.8}\text{O}_4$	1.77	1.11	0.12
$\text{Co}_{1.2}\text{Ge}_{0.2}\text{Fe}_{1.6}\text{O}_4$	1.57	1.21	0.22
$\text{Co}_{1.3}\text{Ge}_{0.3}\text{Fe}_{1.4}\text{O}_4$	1.29	1.33	0.38
$\text{Co}_{1.4}\text{Ge}_{0.4}\text{Fe}_{1.2}\text{O}_4$	1.10	1.43	0.47

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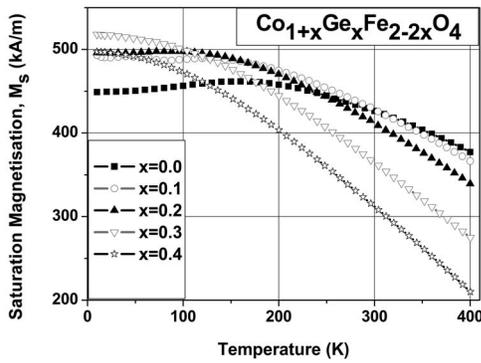


FIG. 1. The variation in technical saturation magnetization with temperature.

Symmetric magnetic hysteresis loops were measured with a SQUID magnetometer for temperatures 10, 50, 100, 150, 200, 250, 300, 350, and 400 K using a maximum applied field of $\mu_0 H = 5$ T.

For calculation of anisotropy, the high field regions of the M - H loops were fitted to the *Law of Approach* to saturation.⁹ The underlying assumption is that this high field regime represents the processes of reversible rotation of magnetization against anisotropy and forced magnetization. According to the *Law of Approach*, the high field regions ($H \gg H_{\text{coercivity}}$) of M - H loops can be described by

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

where M is the magnetization, M_s is the saturation magnetization, H is the applied field, κ is the forced magnetization coefficient that describes the linear increase in spontaneous magnetization at high fields, and K_1 is the first order cubic anisotropy coefficient. The constant $8/105$ is specific to cubic anisotropy of randomly oriented polycrystalline materials. At temperatures above 150 K, data from the field region $\mu_0 H \geq 1$ T were fitted to Eq. (1) to determine the values of parameters M_s , K_1 , and κ . At temperatures below 150 K, the field range for fitting was restricted to $\mu_0 H \geq 2$ T, and, in some cases, the forced magnetization term was set to zero, i.e., $\kappa = 0$, with M_s and K_1 being the only fitting parameters (see discussion below).

III. DISCUSSION

The analysis of temperature dependence of cubic anisotropy of germanium/cobalt cosubstituted cobalt ferrite can be divided into two temperature zones, above and below 150 K. Above 150 K, the maximum applied field is sufficiently large compared to the anisotropy field so as to give good approach to saturation and good fits. The anisotropy of all samples was observed to increase as the temperature decreased. This is so because during cooling, as we move further away from the Curie temperature of these samples, the ratio of exchange interaction to thermal energy increases, which contributes to the increase in anisotropy. As the temperature was reduced from 400 K, the cubic anisotropy for every sample increased slowly at first and steeply below a certain temperature. As can be seen in Fig. 2, the region of steep increase in K_1

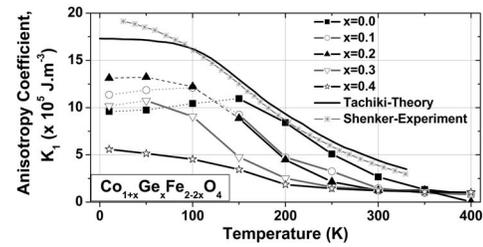


FIG. 2. Temperature dependence of cubic anisotropy coefficient K_1 calculated by fitting the experimental data to *Law of Approach* for $\text{Co}_{1+x}\text{Ge}_x\text{Fe}_{2-2x}\text{O}_4$. Experimental data (Ref. 11) marked as Shenker experiment and theoretically calculated data (Ref. 12) marked as Tachiki theory are presented for comparison.

moved to lower temperatures as the Ge/Co ratio increased from $x=0.0$ to $x=0.4$. It is possible that this effect is correlated with the decrease in Curie temperature of Ge/Co cosubstituted cobalt ferrite with increasing germanium/cobalt ratio.

Below 150 K, the first order magnetocrystalline cubic anisotropy coefficient K_1 appears to decrease with decreasing temperature for CoFe_2O_4 below 150 K, for $\text{Co}_{1.1}\text{Ge}_{0.1}\text{Fe}_{1.8}\text{O}_4$ below 100 K, and for $\text{Co}_{1.2}\text{Ge}_{0.2}\text{Fe}_{1.6}\text{O}_4$ and $\text{Co}_{1.3}\text{Ge}_{0.3}\text{Fe}_{1.4}\text{O}_4$ below 50 K. This apparent decrease can be explained by the presence of anisotropy fields higher than the applied field of $\mu_0 H = 5$ T. This high anisotropy prevents the rotation against it, therefore, causing the apparent saturation magnetization to decrease for CoFe_2O_4 below 160 K, for $\text{Co}_{1.1}\text{Ge}_{0.1}\text{Fe}_{1.8}\text{O}_4$ below 128 K, and for $\text{Co}_{1.2}\text{Ge}_{0.2}\text{Fe}_{1.6}\text{O}_4$ below 78 K, and preventing from complete saturation being reached in these cases (see Fig. 1). The estimated value of anisotropy field $H_k = 2K_1/(\mu_0 M)$ (Ref. 10) for pure cobalt ferrite at 150 K is 4.8 T and is expected to rise above the maximum applied field of 5 T at temperatures below 150 K. Therefore, in these cases, the anisotropy coefficient could not be calculated accurately by fitting the data available to the *Law of Approach* even using special adjustment procedures.⁶ As anisotropy field increased significantly close to 150 K, the region of hysteresis loop where rotation of magnetization against anisotropy takes place shifts to higher field values; therefore, the field range for fitting was restricted to $\mu_0 H \geq 2$ T. Additionally, the force magnetization coefficient was set to zero, i.e., $\kappa = 0$, as in the presence of such high anisotropy fields, the maximum applied field of $\mu_0 H = 5$ T was not sufficient to cause forced magnetization, but rather is still rotating magnetization against the high anisotropy field. Despite these adjustment procedures the values of anisotropy coefficient K_1 , calculated with $\kappa = 0$, are suspect and are connected with dotted lines in Fig. 2. The results from Shenker,¹¹ who determined cubic anisotropy of CoFe_2O_4 using single crystals and torque measurements near their easy axes, support our hypothesis of high anisotropy fields. Additionally, the room temperature value of K_1 for CoFe_2O_4 we determined ($K_1 = 2.66 \times 10^5 \text{ J m}^{-3}$) is consistent with the theoretical predictions made by Tachiki.¹²

As can be seen from Fig. 1, the sample with Ge concentration of $x=0.1$ has higher technical saturation magnetization than pure cobalt ferrite at room temperature. Furthermore, the extrapolated 0 K saturation magnetization $M(0 \text{ K})$ appears to increase initially as we substitute Ge/Co into co-

balt ferrite (for $x=0.1, 0.2$, and 0.3) and then it reduces with high concentration of Ge ($x=0.4$). This indicates that at least initially, the Ge^{4+} ions substitute predominantly into the tetrahedral sites in the inverse spinel structure. This increase in $M(0\text{ K})$ can be understood by considering the structure of the ferrimagnetic cubic spinels and the fact that at least initially the Ge^{4+} ions substitute predominantly into the tetrahedral sites in the inverse spinel structure. In a spinel structure, there are twice as many octahedral sites as tetrahedral sites, and the moments on the octahedral sites and tetrahedral sites couple antiparallel. Thus the net moment is $M_{\text{oct}} - M_{\text{tet}}$. Pure cobalt ferrite is an inverse spinel, meaning that Co^{2+} has an energetic preference for the octahedral sites; however, it tends not to be 100% inverse, meaning that some smaller amount of Co does reside on the tetrahedral sites. Ge^{4+} , on the other hand, is expected to have a natural preference for the tetrahedral sites due to its tetravalence and tendency toward sp^3 hybridization.¹³ So although in $\text{Ge}^{4+}/\text{Co}^{2+}$ cosubstitution for Fe^{3+} much of the Co^{2+} might be substituting into the octahedral sites and decreasing M_{oct} by a little, most of the Ge^{4+} indeed appears to be substituting into the tetrahedral sites, decreasing M_{tet} by much more (since Ge^{4+} has no magnetic moment). Thus the net moment goes up. For high content of Ge ($x=0.4$), $M(0\text{ K})$ appears to decrease again. This could be due to either some of the additional Ge^{4+} substituting into the octahedral sites or due to decrease in the tetrahedral-octahedral exchange coupling to the point that a noncollinear spin arrangement occurs.¹⁴

The substitution of Ge^{4+} reduces the exchange coupling between the octahedral and tetrahedral sites, as can be seen from the steep decrease in Curie temperature with Ge content.⁸ It is probable that this reduction in exchange coupling is responsible for the reduction in the magnitude of magnetic anisotropy, despite the fact that upon Ge/Co cosubstitution, the amount of Co in the octahedral sites most likely increases. The crystalline anisotropy in cobalt ferrite acts like the spring constant against which applied field is acting while producing magnetostriction. Thus, with reduction in anisotropy, the strain derivative (i.e., rate of change in magnetostrictive strain with applied field) increases.¹⁵ This has been indeed observed in the case of Ge/Co cosubstitution.⁸

As opposed to all our previously investigated substitutions of Mn^{3+} ,³ Cr^{3+} ,⁴ and Ga^{3+} (Ref. 7) for Fe^{3+} in cobalt ferrite, for small amounts of Ge/Co cosubstitution ($x=0.1$), the maximum magnetostriction actually increases, rather than decreasing, and then falls off initially more slowly.⁸ This is likely due to increased amount of Co^{2+} in the octahedral sites. This combination of both increasing strain derivative and increasing magnetostriction amplitude with small amounts of Ge/Co cosubstitution makes this material series favorable out of those we have investigated for stress sensor and actuator applications.

IV. SUMMARY AND CONCLUSION

The temperature dependence of magnetic properties of a series of Ge/Co cosubstituted cobalt ferrite with a general

formula of $\text{Co}_{1+x}\text{Ge}_x\text{Fe}_{2-2x}\text{O}_4$ has been measured within a temperature range of 10–400 K. The first order cubic anisotropy coefficient K_1 was calculated by fitting the high field regimes of the magnetization curves to the Law of Approach to saturation. K_1 was observed to increase in magnitude with decrease in temperature with the region of steep increase coming at progressively lower temperatures with increasing Ge/Co substitution. The anisotropy of Ge/Co cosubstituted cobalt ferrite was seen to decrease with increasing germanium concentration at all temperatures. The saturation magnetization at 10 K was seen to increase with germanium concentration for $0 \leq x \leq 0.3$, indicating that for these compositions, Ge^{4+} substitutes predominantly into the tetrahedral sites. It was found that in certain cases of low temperature, the anisotropy of samples with germanium concentration of $x=0, 0.1, 0.2$, and 0.3 was so high that it prevents complete approach to saturation in the presence of maximum applied field of 5 T. For Ge/Co cosubstituted compositions in the region of $\text{Co}_{1.1}\text{Ge}_{0.1}\text{Fe}_{1.8}\text{O}_4$, the combination of higher magnetostrictive strain derivative brought about by lower anisotropy than pure cobalt ferrite and the increased maximum magnetostriction make this material a favorable candidate for stress sensor and actuator applications.

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