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Magnetic and magnetoelastic properties of Cr-substituted cobalt ferrite

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We have investigated the magnetic and magnetoelastic properties of a series of Cr-substituted cobalt ferrite $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.0-0.79$) samples. Substitution of Cr for some of the Fe in cobalt ferrite reduced the Curie temperature, and the effect is more pronounced than that observed in Mn-substituted cobalt ferrite samples. Cr substitution also caused the maximum magnetostriction to decrease at a greater rate than substitution of the same amount of Mn. The maximum of the strain derivative, $d\lambda/dH$, was reached for $x=0.38$. The behavior of the Curie temperature of Cr-substituted and Mn-substituted cobalt ferrites has been analyzed using the Néel molecular field model and compared with recent Mössbauer spectroscopy results. © 2007 American Institute of Physics.

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I. INTRODUCTION

Cobalt ferrite possesses interesting physical properties such as high sensitivity of magnetization to applied stress, excellent chemical stability, and a large magneto-optic effect.¹⁻⁴ It has a cubic spinel-type crystal structure, in which the O^{2-} ions form a fcc-like lattice, and the Co^{2+} and Fe^{3+} cations reside in interstitial sites, of which there are two types: tetrahedral (*A* sites) and octahedral (*B* sites). There are 8 tetrahedral sites and 16 octahedral sites in the unit cell. If all the cobalt resides in the tetrahedral (*A*) sites the crystal structure is known as *normal cubic spinel*, whereas if all the cobalt resides in the octahedral (*B*) sites the crystal structure is known as *inverse cubic spinel*. In practice the distribution of cobalt among the two different types of sites lies between these two extremes. The Co^{2+} ions in cobalt ferrite are generally reported to show a preference for the octahedral (*B*) sites, but they do not exclusively reside in the octahedral (*B*) sites, and the distribution is reported to depend on thermal treatment.⁵

The magnetic and magnetoelastic properties of ferrites are dependent on exchange interactions, and the latter depend on how the cations are distributed among the two sublattices.⁶⁻⁸ Tailoring the chemical composition of cobalt ferrites allows control of the physical properties, including the temperature dependence of magnetic properties and magnetomechanical hysteresis. Recently cobalt ferrite based composites have received attention because of their high magnetostriction, high sensitivity of magnetic induction to applied stress, chemical stability and low cost.⁹⁻¹² These make the materials attractive for use in magnetoelastic sensors,¹ and as the magnetoelastic component in oxide-based “multiferroic” composites.

A series of Mn-substituted cobalt ferrite $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$

samples has been investigated⁹ with the objective of studying the effects of composition on the magnetic and magnetoelastic properties. It was found that both the Curie temperature and the magnetostriction were reduced by the substitution of Mn for Fe. Mössbauer spectroscopy investigation of Mn-substituted cobalt ferrite showed that Mn goes into the octahedral (*B*) sites and displaces Co onto tetrahedral (*A*) sites.¹⁰

A similar Mössbauer spectroscopy study of Cr-substituted cobalt ferrites showed that Cr^{3+} ions have a stronger preference for the *B* sites than Mn^{3+} .¹¹ Additionally, displacement of Co^{2+} ions onto *A* sites was found to be more prevalent in Cr-substituted cobalt ferrites than in Mn-substituted cobalt ferrites.

In the present study the Curie temperatures and magnetostrictions of a series of Cr-substituted cobalt ferrite samples were measured and compared with those of Mn-substituted cobalt ferrite. The maximum magnetostriction and maximum strain derivative of Cr-substituted cobalt ferrites were determined and compared with those of Mn-substituted cobalt ferrites.

II. SAMPLE DETAILS

A series of polycrystalline Cr-substituted cobalt ferrite samples with target compositions of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ (where x ranges from 0 to 0.8) was prepared by standard powder ceramic techniques^{1,9} using Fe_2O_3 , Cr_2O_3 , and Co_3O_4 powders as precursors. Samples were calcined twice, sintered in air, and subsequently furnace cooled to room temperature. The final compositions of the sintered samples were found to be close to the target composition, as shown in Table I. Using x-ray powder diffractometry, all samples were determined to be of single phase and to have the cubic spinel structure. Microstructural study using scanning electron microscopy (SEM) showed that all the sintered samples had a homogeneous microstructure with similar grain sizes of the order of 10 μm . The Curie temperature T_C was determined by mea-

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TABLE I. Target compositions of a series of Cr-substituted cobalt ferrite samples, and the final compositions determined using energy-dispersive x-ray spectroscopy (EDX) in a SEM.

Target composition	Final composition by EDX		
	Co	Cr	Fe
CoFe _{2.0} O ₄	0.95	...	2.05
CoCr _{0.2} Fe _{1.8} O ₄	0.94	0.14	1.92
CoCr _{0.4} Fe _{1.6} O ₄	1.00	0.38	1.62
CoCr _{0.6} Fe _{1.4} O ₄	0.95	0.53	1.52
CoCr _{0.8} Fe _{1.2} O ₄	0.95	0.79	1.26

suring magnetization as a function of temperature while cooling through the transition in a vibrating sample magnetometer (VSM) under a dc field of 7.96 kA/m (100 Oe). Magnetostriction as a function of applied field at room temperature was measured using the strain gauge method.

III. EXPERIMENTAL RESULTS

Figure 1 shows the Curie temperatures T_C of the CoCr_xFe_{2-x}O₄ samples as a function of the substituent content x . The data are compared with the Curie temperatures T_C of CoMn_xFe_{2-x}O₄ obtained previously.⁹ It can be seen that the Curie temperature T_C decreases almost linearly with increasing Cr content in CoCr_xFe_{2-x}O₄. This means that magnetic properties and their temperature dependence can be controlled through selection of chemical composition.

This behavior of Curie temperature T_C as a function of the level of substitution can be explained by the Néel molecular field model.¹³ According to this model, the A - B intersublattice superexchange interactions are dominant compared with those of A - A or B - B intrasublattice superexchange interactions. Thus, the Curie temperature of the ferrites is determined principally by the strength of A - B interactions and any alterations of this, caused by cation substitution or displacement of Co²⁺ from the B sites to the A sites, will have significant effects on the Curie temperature. The strength of A - B intersublattice superexchange interac-

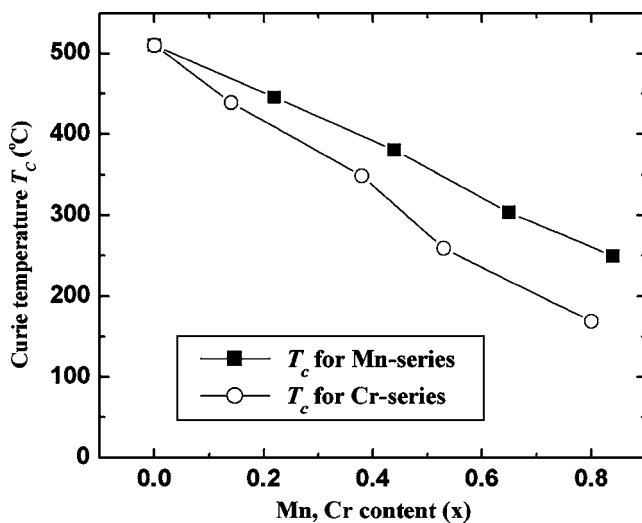


FIG. 1. Curie temperatures T_C of CoCr_xFe_{2-x}O₄ and CoMn_xFe_{2-x}O₄ samples as a function of the substituted content x .

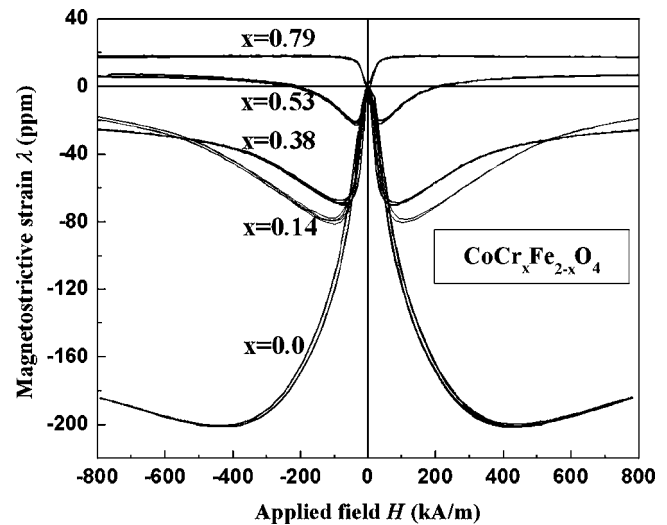


FIG. 2. Magnetostriction curves of CoCr_xFe_{2-x}O₄ samples.

tion is a function of the Fe³⁺_A-O²⁻-Fe³⁺_B superexchange linkage mediated through the oxygen.¹⁴ This in turn depends on the number of Fe³⁺ ions in the formula unit and their distribution among the A sites and B sites. Recent Mössbauer spectroscopy investigation of CoCr_xFe_{2-x}O₄ confirms that Cr³⁺ ions have a strong B -site preference and replace Fe³⁺ ions, which are superexchange coupled to six next-nearest neighbors at the A sites.⁵ This results in decreasing the strength of the A - B intersublattice superexchange interactions, thus decreasing the Curie temperature of CoCr_xFe_{2-x}O₄. The rate of change of Curie temperature dT_C/dx is greater for CoCr_xFe_{2-x}O₄ than for CoMn_xFe_{2-x}O₄, as shown in Fig. 1. This indicates that the strength of overall A - B intersublattice superexchange coupling of Mn-substituted cobalt ferrite is larger than that of Cr-substituted cobalt ferrite for the same amount x of substituent. It can be inferred from the Mössbauer spectroscopy results that the Cr³⁺ ions have a stronger B -site preference than the Mn³⁺ ions, and are more effective in displacing Co²⁺ ions from the B sites to the A sites^{10,11} (each of which is superexchange linked to 12 next-nearest neighbors at the B sites).⁵ This means that not only are Fe³⁺ ions on B sites being replaced by Cr³⁺ ions as a result of compositional substitution but those Fe³⁺ ions that remain at B sites are superexchange linked to fewer A -site Fe³⁺ ions, as Co²⁺ ions are displaced to A sites. Thus the Curie temperature decreases more with Cr substitution than with Mn substitution.

Chromium substitution for iron in cobalt ferrite was also found to have a strong effect on magnetostriction. As shown in Fig. 2, the magnitude of magnetostriction decreased with increasing Cr content for x up to 0.53. For $x=0.53$, magnetostriction became positive for fields above 200 kA/m (2.5 kOe), and for $x=0.79$, magnetostriction was positive for all fields, as shown in Fig. 2. This is in contrast to the Mn-substituted cobalt ferrite samples, which had negative magnetostriction under applied fields up to 1600 kA/m (20 kOe).⁹ Cr substitution also causes the magnitude of maximum magnetostriction, $|\lambda_{\max}|$, to decrease at a greater rate than for Mn substitution, as shown in Fig. 3.

It is worth mentioning the notable result that substituting

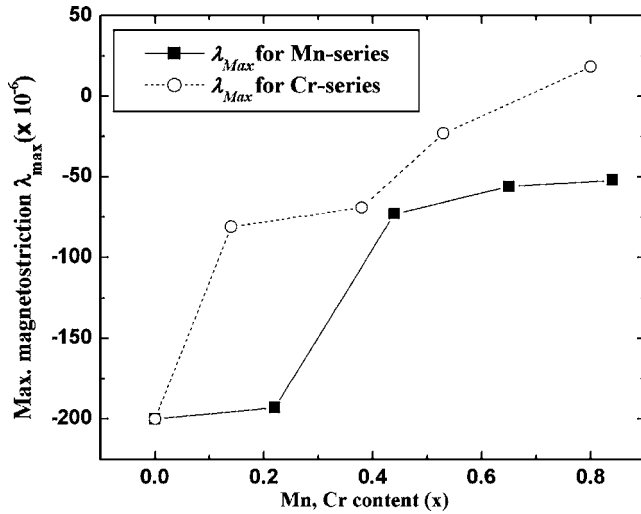


FIG. 3. Plot of maximum magnetostriction λ_{max} of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ and $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ as a function of the substituted content x .

small amounts of Cr for Fe (e.g., $\text{Co}_{1.00}\text{Cr}_{0.38}\text{Fe}_{1.62}\text{O}_4$) increases the magnitude of the maximum strain derivative $|(d\lambda/dH)_{max}|$, as shown in Fig. 4, while the magnetostriction level decreases with Cr content. Similar behavior has been observed in a recent study of Mn-substituted cobalt ferrite $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$ (Fig. 4), although the peak occurs at a somewhat different value of substituent content x (at $x=0.22$ for the Mn-substituted series⁹ and at $x=0.38$ for the Cr-substituted series). The magnitude $|(d\lambda/dH)_{max}|$ of both the Cr-substituted series and the Mn-substituted series is larger than that of pure cobalt ferrite for small amounts of added substituent x (i.e., for x up to 0.38 for Cr-substituted series and for x up to 0.22 for the Mn-substituted series). Furthermore, the peak value of $|(d\lambda/dH)_{max}|$ for the Cr-substituted series is only 20% less than that of the Mn-substituted series, despite the fact that the Curie temperature T_C is 100 °C less (350 and 450 °C for the $\text{Co}_{1.00}\text{Cr}_{0.38}\text{Fe}_{1.62}\text{O}_4$ and $\text{Co}_{0.95}\text{Mn}_{0.22}\text{Fe}_{1.83}\text{O}_4$, respectively). According to a well known thermodynamic relationship, $(d\lambda/dH)_\sigma$ is related to

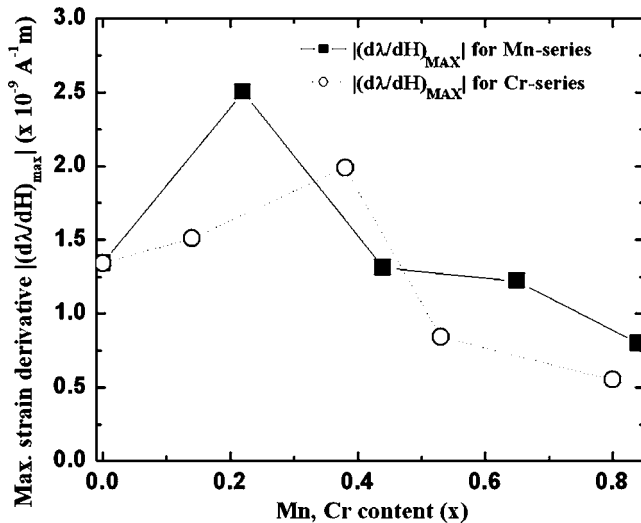


FIG. 4. Dependence of the magnitude of maximum strain derivative $|(d\lambda/dH)_{max}|$ on the Cr and Mn contents.

the stress sensitivity of induction $(dB/d\sigma)_H$ for reversible processes under small applied field and stress.¹⁵ The strain derivative $(d\lambda/dH)_\sigma$ can therefore be used as a figure of merit of the stress sensitivity of magnetic induction to stress or torque when selecting materials for stress or torque sensor applications. The present experimental results therefore suggest that cobalt ferrites substituted with small amounts of Cr or Mn for Fe are promising candidate materials for use in magnetoelastic sensors due to their enhanced strain derivatives $(d\lambda/dH)_{max}$.

IV. DISCUSSION

Pure cobalt ferrite is known to have $\langle 100 \rangle$ easy axes ($K_1 > 0$), $\lambda_{100} < 0 < \lambda_{111}$, and $|\lambda_{100}| \gg |\lambda_{111}|$.¹⁶ It appears that Cr substitution reduces the magnitudes of both λ_{100} and λ_{111} of cobalt ferrite but also progressively decreases λ_{100} relative to λ_{111} . For polycrystalline materials with no texture (preferred crystallographic orientation), such as these samples, the high-field saturation magnetostriction is given by $\lambda_s = 2/5(\lambda_{100}) + 3/5(\lambda_{111})$. Thus for $\text{Co}_{0.95}\text{Cr}_{0.53}\text{Fe}_{1.52}\text{O}_4$, it is probable that K_1 remains positive, $\lambda_{100} < 0 < \lambda_{111}$ but $|\lambda_{100}| < 3/2|\lambda_{111}|$. This would account for the observed reversal in sign of the magnetostrictive strain at high fields when domain magnetization is rotated away from the local easy directions closest to the applied field, toward the applied field direction. For $x=0.79$, apparently $|\lambda_{100}|$ becomes negligible compared to $|\lambda_{111}|$ so that the bulk magnetostriction is positive for all fields, as shown in Fig. 2. It appears therefore that Cr substitution has a stronger effect on λ_{100} than on λ_{111} .

It has been suggested that the strain derivative and hence the stress sensitivity of magnetic induction depend on both the magnetostriction and anisotropy.¹⁷ For untextured polycrystalline materials, domain magnetization processes are expected to occur more readily under the influence of applied magnetic field or stress for a material with a smaller magneto-crystalline anisotropy. This results in a larger magnetostrictive strain for a given change in applied field (and hence a larger strain derivative) or a larger magnetization change for a given applied stress (and hence higher stress sensitivity). We have found in a recent study that for a fixed temperature the magnetic anisotropy of Cr-substituted cobalt ferrites decreases with increasing Cr content.¹⁸ This could account for the observed increased strain derivatives for the $\text{Co}_{1.00}\text{Cr}_{0.38}\text{Fe}_{1.62}\text{O}_4$ and $\text{Co}_{0.94}\text{Cr}_{0.14}\text{Fe}_{1.92}\text{O}_4$ samples.

Both Cr^{3+} and Mn^{3+} are known to have preferences for the octahedral or B sites in the ferrite structure,¹⁹ and Co^{2+} has a stronger preference for the octahedral sites than Fe^{3+} in pure cobalt ferrite. However, Mössbauer spectroscopy investigations of these two series of samples indicated that substitution of Cr or Mn for Fe in cobalt ferrite is not just a simple substitution of one cation for the other on the octahedral sites.^{10,11} Rather, it appears that Cr or Mn substitutes into octahedral sites, and also displaces some Co to tetrahedral sites. Furthermore, Cr substitution is more effective than Mn in displacing Co. Thus the present observation that Cr substitution decreased the magnitude of maximum magnetostriction more than an equivalent amount of Mn substitution is

consistent with the Mössbauer results, assuming that magnetostriction is determined largely by the number of Co ions located at octahedral sites.

V. CONCLUSIONS

The Curie temperature and magnetoelastic properties of a series of Cr-substituted cobalt ferrites have been investigated and compared to those of Mn-substituted cobalt ferrite. Substitution of Cr for some of the Fe in cobalt ferrite was found to decrease the Curie temperature and the rate of decrease was greater than that observed for similar levels of Mn substitution. Cr substitution also decreased the maximum magnitude of magnetostriction at a rate greater than for Mn substitution. These results are consistent with the Mössbauer results which indicate that Cr³⁺ ions substitute into the octahedral sites with stronger preference than Mn³⁺ and displace the Co²⁺ ions to tetrahedral sites more effectively than Mn³⁺ ions do. For small amounts of substituent, both Cr-substituted and Mn-substituted cobalt ferrites have maximum strain derivatives $|(d\lambda/dH)_{\max}|$ greater than that of pure cobalt ferrite, and therefore show promise for magnetoelastic sensing applications.

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