

# Investigation of Ga substitution in cobalt ferrite ( $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$ ) using Mossbauer spectroscopy

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Ga-substituted cobalt ferrite oxides show promise as high magnetostriction, high sensitivity magnetoelastic materials for sensor and actuator applications, but their atomic-level behavior is not yet well understood. In this study, the magnetic environments of the Fe atoms in Ga-substituted cobalt ferrite have been investigated using Mossbauer spectroscopy. A series of five powder samples with  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  compositions ( $x=0.0-0.8$ ) was investigated using transmission geometry. Results show two distinct six-line hyperfine patterns, which are identified as Fe in *A* (tetrahedral) and *B* (octahedral) spinel sites. Increasing Ga concentration is seen to decrease the hyperfine field strength for both *A* and *B* sites, as well as increasing the width of those distributions, consistent with the nonmagnetic nature of  $\text{Ga}^{3+}$  ions. Effects are more pronounced for the *B* sites than the *A* sites. Results for Ga substitution show more pronounced effects than for previous studies with  $\text{Cr}^{3+}$  or  $\text{Mn}^{3+}$  substitution: the hyperfine fields decrease and distribution widths increase at greater rates, and the differences between *A* and *B* site behavior are more pronounced. Results indicate that at least for the lower Ga concentrations, the  $\text{Ga}^{3+}$  ions substitute predominantly into the *A* sites, in contrast to  $\text{Cr}^{3+}$  and  $\text{Mn}^{3+}$  which substitute into the *B* sites. This interpretation is supported by measurements of magnetization at low temperatures. © 2008 American Institute of Physics.

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## INTRODUCTION

The development of cobalt ferrite-based materials has received recent attention for the potential applicability of such materials as magnetoelastic sensors and actuators, and as the magnetoelastic component in composite “multiferroics.”<sup>1,2</sup> Substitution of elements such as Mn or Cr for some of the Fe has shown promise of adjusting the magnetic and magnetoelastic properties of these materials through control of chemical composition.<sup>3,4</sup> In order to fully enable the practical applications of these compounds, a more complete family of materials is needed, such that the desired properties can be tailored to a specific application. In the present study, we report on the magnetic characterization of the series of Ga-substituted cobalt ferrites  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  ( $x=0.0-0.8$ ) as a function of gallium concentration using transmission Mossbauer spectroscopy. The effects of this substitution were expected to be different for Mn and Cr substitution.<sup>5-7</sup>

## EXPERIMENTAL DETAILS

The samples used in this study were prepared at Ames Laboratory, USDOE. The samples were of the composition  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  (where  $x=0.0-0.8$ ). Standard powder ceramic techniques were employed using  $\text{Fe}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{Co}_3\text{O}_4$  powders as precursors. The powders were calcined

twice, sintered at 1350 °C for 24 h, and furnace cooled (see Ref. 7 for details). The final compositions of the samples were determined by energy-dispersive x-ray spectroscopy, and all samples were confirmed by x-ray powder diffraction to be single phase and have the cubic spinel structure.<sup>7</sup> Samples were prepared for transmission Mossbauer measurements by mounting a layer of powder between layers of plastic tape and stacking several layers of sandwiched material. The Mossbauer system utilized a 20 mCi  $\text{Co}^{57}(\text{Rh})$  source, linear drive operating in constant acceleration mode, and a 1024 channel multichannel analyzer. Details of the Mossbauer spectroscopy system can be found in Ref. 8.

## RESULTS AND DISCUSSION

In Fig. 1, Mossbauer transmission spectra of the five samples are shown, with gallium concentration increasing from bottom to top ( $x=0.0, 0.2, 0.4, 0.6$ , and  $0.8$ ). The spectra show the presence of two distinct hyperfine sextets. This indicates the presence of two different types of ferromagnetic Fe atoms in the material, which are identified as Fe in the *A* (tetrahedral) and *B* (octahedral) sites of the spinel structure. The spectra show a behavior that is observed to be qualitatively similar to that of the Cr- and Mn-substituted cobalt ferrites:<sup>8,9</sup> as the Ga concentration increases, the line spacing (indicative of the magnetic hyperfine field at the Fe nuclei and related to the exchange coupling) can be seen to decrease and the spacing of the two individual sextets that make up

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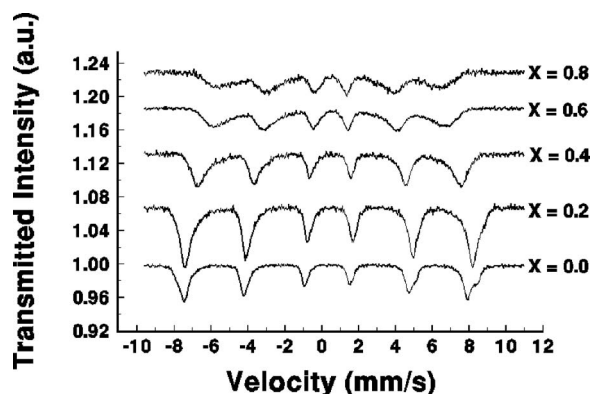


FIG. 1. Raw transmission Mossbauer data for  $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$ , where  $x = 0.0, 0.2, 0.4, 0.6$ , and  $0.8$  (in order from bottom to top).

each spectrum varies relative to one another. Quantitative values for the mean hyperfine field strengths, hyperfine field distribution widths, and isomer shifts of Fe A and B sites in all the samples were calculated by fitting a composite of two hyperfine patterns to each spectrum using WMOSS analysis software. As an example, Fig. 2 shows the results of the fit for the  $\text{CoFe}_{1.4}\text{Ga}_{0.6}\text{O}_4$  sample, including the two individual hyperfine patterns for the A and B sites, the best fit curve (which is their sum), and the experimental data from which they are derived. The results of these analyses are shown in Figs. 3–5, which show the mean hyperfine field strength, hyperfine field distribution width, and isomer shift, respectively, as a function of gallium concentration. The identification of which sextet corresponds to the A sites and which corresponds to the B sites was accomplished by consideration of the isomer shift results, and the hyperfine field distribution widths and hyperfine field strengths for  $x=0$ , as outlined in Refs. 8 and 9.

We now consider the effect of Ga substitution on hyperfine field strength and distribution width. Both A-site and B-site hyperfine fields are observed to decrease with increasing Ga content, with B decreasing faster than A (see Fig. 3). In a similar manner (see Fig. 4), the hyperfine field distribution width increases with increasing Ga content, with the B-site distribution width increasing faster than A. Both the A-site and B-site hyperfine fields decrease at a faster rate for Ga substitution than they do for Mn substitution<sup>8</sup> or even Cr

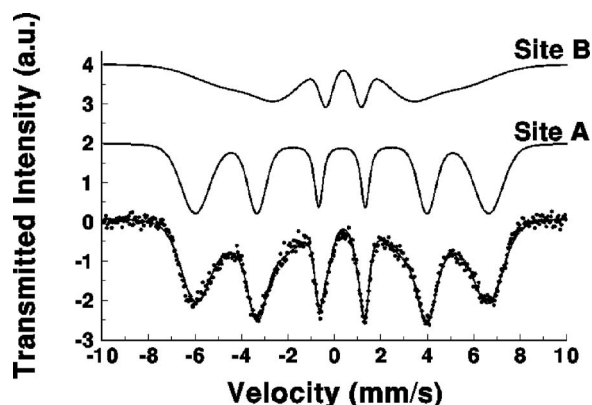


FIG. 2. Experimental Mossbauer data and fit with two six-line hyperfine patterns for  $\text{CoFe}_{1.4}\text{Ga}_{0.6}\text{O}_4$  ( $x=0.6$ ).

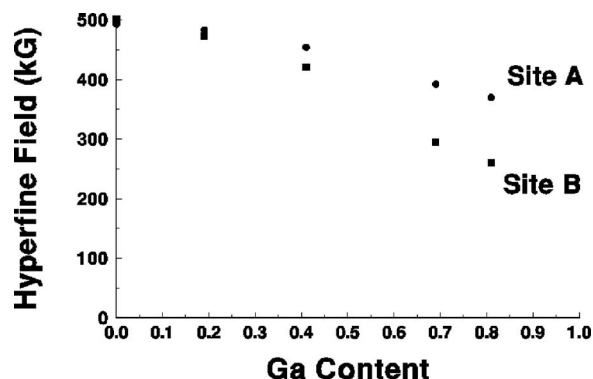


FIG. 3. Hyperfine field strength as a function of Ga content ( $x$ ) in  $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$ . (Identification of A and B sites is discussed in the text.)

substitution,<sup>9</sup> and the hyperfine field distribution widths increase at a faster rate. Furthermore, the difference in hyperfine field and hyperfine field distribution width between the A-sites and B-sites becomes greater for  $\text{Ga}^{3+}$  substitution than for  $\text{Mn}^{3+}$  or  $\text{Cr}^{3+}$  substitution.

The  $\text{Ga}^{3+}$  ion has ten 3d electrons and, thus, no unpaired d electrons, no magnetic moment, and does not participate in superexchange interactions. Therefore, its substitution will, in general, be more disruptive to ferromagnetism than that of the ions  $\text{Mn}^{3+}$  or  $\text{Cr}^{3+}$ , which do have unpaired d electrons and magnetic moments. Furthermore, in some other spinel ferrites [ $\text{MnGa}_x\text{Fe}_{2-x}\text{O}_4$ ,<sup>5</sup>  $\text{Ga}_x\text{Fe}_{1-x}\text{NiCrO}_4$ ,<sup>6</sup> and  $\text{MgGa}_x\text{Al}_{2-x}\text{O}_4$  (Ref. 10)], substituted  $\text{Ga}^{3+}$  has been observed to show a preference for the tetrahedral sites, although the predictions for the substituted cobalt ferrite system are not entirely clear, as  $\text{Ga}^{3+}$  has also been reported to show a less strong A-site preference than  $\text{Fe}^{3+}$ .<sup>11</sup> The predominant superexchange coupling in these spinel ferrites is generally the A-B coupling, which is antiferromagnetic. Moreover, each A-site cation in cobalt ferrite is superexchange linked to 12 B-site next-nearest neighbor cations, whereas each B-site cation is superexchange linked to only six next-nearest neighbor A-site cations.

In view of the above, it appears that  $\text{Ga}^{3+}$  substitutes predominantly into the A sites in the substituted cobalt ferrites  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$ . This would explain the predominant decrease of the B-site hyperfine field and increase of B-site distribution width (since B-site  $\text{Fe}^{3+}$  ions are superexchange

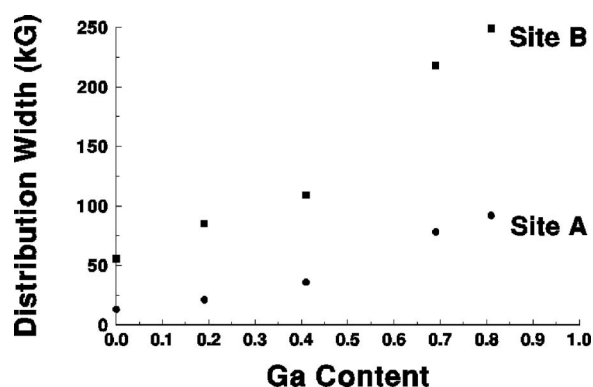


FIG. 4. Hyperfine distribution width as a function of Ga content ( $x$ ) in  $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$ . (Identification of A and B sites is discussed in the text.)

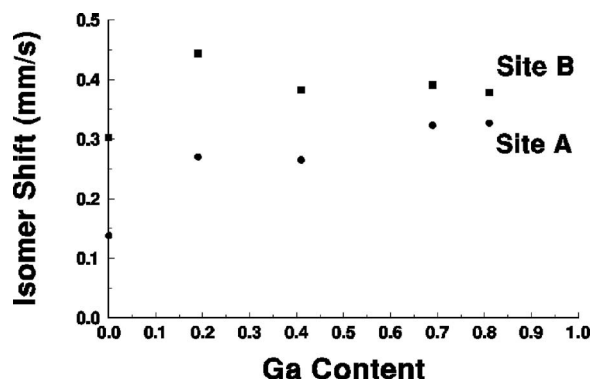


FIG. 5. Isomer shift as a function of Ga content ( $x$ ) in  $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$ . (Identification of  $A$  and  $B$  sites is discussed in the text.)

coupled to six  $A$ -site cations). In the case of  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$  substitutions, it was observed that  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$  appear to substitute into the  $B$  sites and displace some of the  $\text{Co}^{2+}$  onto the  $A$  sites.<sup>8,9</sup> In the case of  $\text{Ga}^{3+}$ , a combination of the more-direct substitution onto the  $A$  sites and substitution of a non-magnetic ion decreases the  $B$  site hyperfine field and increases the  $B$ -site distribution width even more rapidly. Measurements of the saturation magnetization  $M_s$  at low temperature (where thermal disorder is minimized) support this hypothesis. They show that at least for the smaller amounts of substituted  $\text{Ga}^{3+}$ , the overall magnetization increases relative to pure cobalt ferrite upon substitution of  $\text{Ga}^{3+}$  for  $\text{Fe}^{3+}$ .<sup>12</sup> Since  $\text{Ga}^{3+}$  is nonmagnetic, and the  $A$ -site and  $B$ -site moments couple antiparallel (and remembering that there are twice as many  $B$  sites as  $A$  sites), this supports the idea that  $\text{Ga}^{3+}$  substitutes preferentially into the  $A$  sites. Further support is provided by the observation that substitution of  $\text{Ga}^{3+}$  for  $\text{Fe}^{3+}$  in cobalt ferrite has been observed to decrease the Curie temperature at a faster rate than of  $\text{Mn}^{3+}$  or  $\text{Cr}^{3+}$  (see discussion in Ref. 7).

The  $A$ -site hyperfine field is also observed to decrease, and hyperfine field distribution width increases with increasing substitution of  $\text{Ga}^{3+}$ . It is not clear at present whether this is due to some minority fraction of the  $\text{Ga}^{3+}$  substituting into the  $B$  sites, whether  $\text{Ga}^{3+}$  substitution into the  $A$  sites is causing some of the  $\text{Co}^{2+}$  to be displaced onto the  $B$ -sites, or whether it is due to the fact that as the  $\text{Ga}^{3+}$  substitution onto the  $A$  sites causes the  $B$  site spins to be less strongly superexchange coupled and show larger variation, the remaining  $\text{Fe}^{3+}$  ions on the  $A$  sites that are coupled to them could thus see a reduced hyperfine field and show a wider distribution. This will require further investigation to elucidate.

## CONCLUSIONS

The effects of Ga concentration on the magnetic environments of Fe in Ga-substituted cobalt ferrites ( $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$ , where  $x$  ranges from 0.0 to 0.8) have been studied using Mossbauer spectroscopy. Distinct contributions due to the  $A$  sites (tetrahedral) and  $B$  sites (octahedral) can be

identified in the Mossbauer spectra. The results indicate a reduction of magnetic hyperfine field strength and an increase of magnetic hyperfine field distribution as Ga is substituted for Fe in  $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$ . The effect is more pronounced for the  $B$  sites than for the  $A$  sites. The amounts of hyperfine field reduction and distribution width increase have been shown to be greater for Ga-substituted than for Cr- or Mn-substituted cobalt ferrites. Furthermore, the difference between  $A$ -site and  $B$ -site hyperfine fields decreases and distribution width increase is also greater for the Ga-substituted cobalt ferrites. Results are consistent with a model in which  $\text{Ga}^{3+}$  substitutes preferentially into the  $A$  sites, rather than the  $B$  site preference of  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$ . This model is supported by low temperature  $M_s$  measurements and Curie temperature measurements. Such characterizations and further measurements and analysis should help indicate how cation substitution and cation site occupancy affect the bulk magnetic and magnetoelastic properties of this family of materials, providing valuable information for future material studies and applications of these materials.

## ACKNOWLEDGMENTS

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