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Investigation of Cr substitution in Co ferrite ($CoCr_xFe_{2-x}O_4$) using Mossbauer spectroscopy

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Substitution of other metals for Fe in cobalt ferrite has been proposed as a method to tailor the magnetic and magnetoelastic properties for sensor and actuator applications [H. Zheng *et al.*, Science **303**, 661 (2004)]. However, to understand the effect of Cr substitution, one needs atomic-level information on the local environments and interactions of the transition-metal ions. In this study, Mossbauer spectroscopy was used to investigate the local environments of the Fe atoms in these materials. A series of five powder samples with compositions $CoCr_xFe_{2-x}O_4$ ($x=0.0$ to 0.8) was investigated using transmission geometry. Results show two distinct six-line hyperfine patterns, indicating Fe in *A* and *B* spinel sites. Increasing Cr concentration is seen to decrease the hyperfine field strength for both *A* and *B* sites, as well as increasing the width of those distributions. Results for Cr substitution show generally similar behavior to a prior study using Mn; however, Cr substitution has more pronounced effects: the hyperfine fields decrease and distribution widths increase at greater rates for Cr substitution, and the differences between *A* and *B* site behavior are more pronounced. Results are consistent with a model in which Cr has an even stronger *B*-site preference than Mn, and displaces more of the Co from the *B* to the *A* sites. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2167051]

INTRODUCTION

Cobalt ferrites and cobalt-ferrite-based composites have received recent attention, as promising materials for magnetomechanical strain sensing and actuating applications, and multiferroic materials.[1,2] Substitution of elements such as manganese or chromium into cobalt ferrites has been proposed, in order to tailor the magnetic and magnetomechanical properties of such materials.[3] Chromium-substituted cobalt ferrites are of particular interest in that the Cr^{3+} ions are reported to have a very strong preference for the *B* sites of the spinel structure of the ferrites,[4,5] stronger yet than the *B*-site preference of Mn^{3+} (the subject of our study in Ref. 6), and thus should offer an illuminating comparison. A few previous investigations of chromium cobalt ferrites have been reported, but they mainly concentrated on the Cr-rich side (i.e., $1<x<2$).[7,8] One that did use Mossbauer spectroscopy to study this series[5] got results that contradict many previous reported measurements for pure cobalt ferrite [e.g., Refs. 6, 9, and 10]. They suggested canted rather than collinear spin arrangements for even pure cobalt ferrite, possibly due to their not being able to saturate the sample at low temperatures due to the high anisotropy field $H_k \gg H_{\text{applied}}$.[11] In the present study, we report on the magnetic characterization of cobalt-rich chromium-substituted cobalt ferrite powders ($CoFe_{2-x}Cr_xO_4$ for $x=0.0$ to 0.8) as a function of chromium concentration using transmission Mossbauer spectroscopy.

EXPERIMENTAL DETAILS

A series of chromium-substituted cobalt ferrite powder samples with compositions $CoFe_{2-x}Cr_xO_4$ (where *x* ranges from 0.0 to 0.8) were prepared by standard powder ceramic techniques, using Fe_2O_3, Co_3O_4, and Cr_2O_3 powder precursors, and a three-stage process as described in Ref. 6, in which samples were mixed, calcined, reground, calcined, reground, final sintered, and reground, in order to get complete reaction and homogeneous powder samples. Powder x-ray diffractometer (XRD) measurements were performed on all samples in the series. The results confirmed that all samples are single phase, with the cubic spinel structure. Samples were prepared for transmission Mossbauer measurements by mounting a layer of powder between layers of plastic tape. The Mossbauer system utilized a 15 mCi Co^{57}(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. 6.

RESULTS AND DISCUSSION

In Fig. 1 Mossbauer transmission spectra of the five samples are shown, with chromium concentration increasing from bottom to top ($X=0.0$, 0.2, 0.4, 0.6, and 0.8). The spec-

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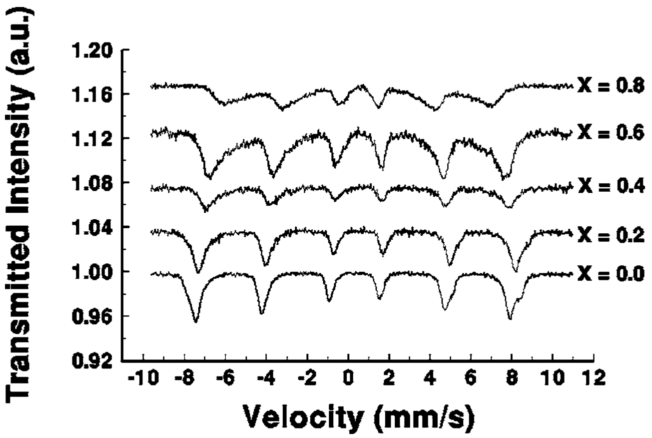

FIG. 1. Raw transmission Mossbauer data for $CoFe_{2-x}Cr_xO_4$ where $x = 0.0, 0.2, 0.4, 0.6$, and 0.8 (in order, bottom to top).

tra show the presence of two distinct hyperfine sextets. This indicates the presence of two different types of ferromagnetic Fe atoms in the structure, 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 Mn-substituted cobalt ferrites:[6] As the Cr concentration increases, the splitting (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 each spectrum vary relative to one another.

Quantitative values for the mean hyperfine field strengths, hyperfine field distribution widths, and isomer shifts of *A*- and *B*-site Fe in all the samples were calculated by fitting a composite of two hyperfine patterns to each spectrum using the WMOSS software, as outlined in Ref. 6. As an example, Fig. 2 shows the results of the fit for the $CoFe_{1.2}Cr_{0.8}O_4$ sample, including the two individual hyperfine patterns, 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 hyperfine field strength, hyperfine field distribution width, and isomer shift, respectively, as a function of chromium concentration. In order to analyze these results in detail we must first identify which pattern corresponds to the *A* sites, and which to the *B* sites. Considering first the isomer shift results, one type of Fe site shows a range of 0.14–0.29 mm/s, while the other type shows a range of 0.30–0.38 mm/s. The expected ranges for Fe^{3+} with oxygen coordination are 0.20–0.30 mm/s for tetrahedral, and 0.30–0.48 mm/s for octahedral.[12] Thus isomer shift results indicate a clear-cut identification of *A* (tetrahedral) and *B* (octahedral) sites. Next, we consider whether this identification appears consistent with the hyperfine field distribution widths and hyperfine field strength (Figs. 4 and 3). Following the model of Sawatzky *et al.*,[9] we would expect the *B*-site distribution width for pure cobalt ferrite (i.e., $x=0.0$) to be greater than the *A*-site width, due to the fact that each *A*-site ion is most strongly superexchange coupled to its 12 next nearest-neighbor *B*-site ions, whereas each *B*-site ion is most strongly superexchange coupled to only its six next-nearest *A*-site ions (see Ref. 6 for more detailed discussion). Thus our identification of *A* and *B* sites is confirmed by the hyperfine field distribution width data. Whether one observes the *A* or *B* site hyperfine field to be larger for pure cobalt ferrite ($x=0.0$) will depend on the details of the site occupancies of the Co and Fe, which will depend on heat treatment.[9] The ratio of integrated areas under the two hyperfine field patterns for the pure cobalt ferrite also appears consistent with our identification of *A* and *B* site contributions.

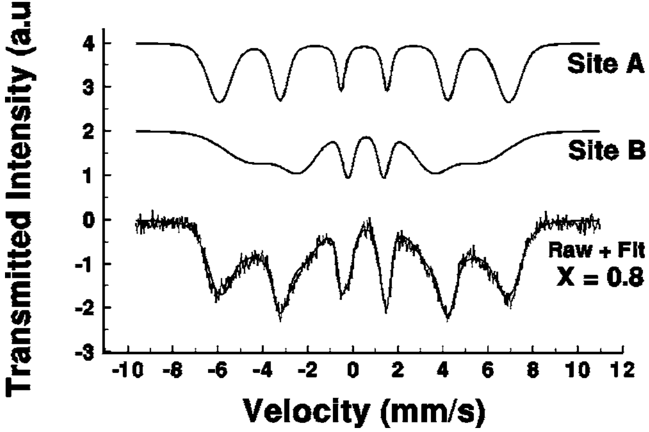

FIG. 2. Experimental Mossbauer data and fit with two six-line hyperfine patterns for $CoFe_{1.2}Cr_{0.8}O_4$ ($x=0.8$).

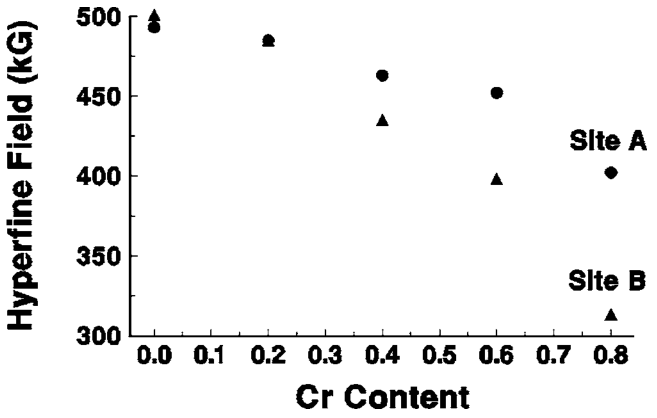

FIG. 3. Hyperfine field strength as a function of Cr content (x) in $CoFe_{2-x}Cr_xO_4$. (Identification of *A* and *B* sites is discussed in the text.)

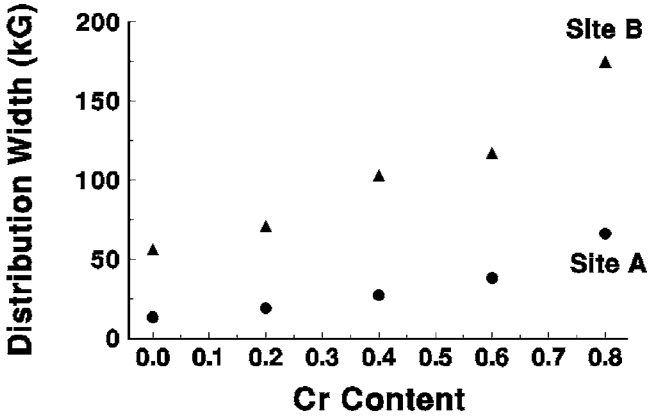

FIG. 4. Hyperfine distribution width as a function of Cr content (x) in $CoFe_{2-x}Cr_xO_4$. (Identification of *A* and *B* sites is discussed in the text.)

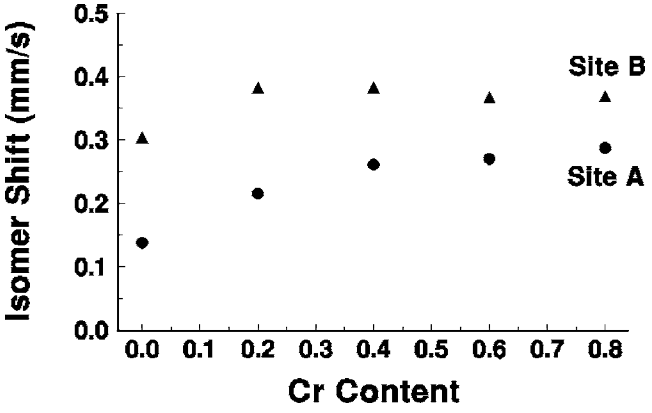

FIG. 5. Isomer shift as a function of Cr content (x) in $CoFe_{2-x}Cr_xO_4$. (Identification of A and B sites is discussed in the text.)

Having identified the A and B site contributions, let us consider the effect of Cr substitution on hyperfine field strength and distribution width. Both A-site and B-site hyperfine fields are observed to decrease with increasing Cr content, with B decreasing faster than A (see Fig. 3). The overall decrease of hyperfine field as a function of Cr content, and the decrease of each of the two sites can be understood assuming Cr^{3+}–O–Fe^{3+} superexchange links are not as strong as Co^{2+}–O–Fe^{3+} or Fe^{3+}–O–Fe^{3+} links, and Co^{2+}–O–Fe^{3+} links are not as strong as Fe^{3+}–O–Fe^{3+} (the latter appears true according to Ref. 9). We know that all the Fe in the structure is Fe^{3+} from the ranges of observed isomer shift values,[12] and in substituting Cr for Fe, we assume that $Cr^{+3}$is substituting for Fe^{+3}. Cr^{3+} is reported to have a very strong B-site preference, stronger even than Mn^{3+}.[4] It appears that Cr is not merely replacing Fe in the B sites (in which case the A-site hyperfine field and distribution width might be expected to be more affected than B, since A-B superexchange coupling is the strongest). Rather, it would appear that Cr substitutes into the B sites and has the effect of displacing Co ions onto the A sites. Each B site Fe is superexchange linked to only six A next-nearest neighbors (compared to each A-site Fe, which is superexchange linked to 12 B next-nearest neighbors), and it is reported that Fe–O–Co superexchange appears weaker than Fe–O–Fe superexchange[9].Thus by this model, B-site hyperfine field would decrease and the distribution width would increase faster than for the A site.

Comparing the effects of Cr substitution for Fe in cobalt ferrite to those of Mn substitution (Ref. 6), we observe that hyperfine field decreases faster with Cr substitution than it does with Mn substitution for both A and B sites, and that the difference between A and B is greater. In a like manner, the hyperfine distribution width increases faster with Cr substitution compared to Mn substitution for both A and B sites, and the difference between A and B is greater. These are consistent with the model of Cr ions substituting into the B sites and displacing Co ions onto the A sites provided Cr is even more effective in displacing Co ions to A sites, and Cr^{3+}–O–Fe^{3+} superexchange links are not as strong as Co^{2+}–O–Fe^{3+} or Fe^{3+}–O–Fe^{3+} links.

CONCLUSIONS

The effects of chromium concentration on the magnetic hyperfine characteristics of Fe in Cr-substituted cobalt ferrites ($CoFe_{2-x}Cr_xO_4$, where x ranges from 0.0 to 0.8) have been studied using Mossbauer spectroscopy. Separate contributions due to the A (tetrahedral) and B (octahedral) sites 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 Cr is substituted for Fe in $CoFe_{2-x}Cr_xO_4$. The amount of hyperfine field reduction has been shown to be greater for Cr-substituted than for Mn-substituted cobalt ferrites, and the increase of hyperfine field distribution width is also greater for Cr-substituted cobalt ferrites. Furthermore, the difference between A-site and B-site hyperfine field and distribution behavior is also greater for the Cr-substituted cobalt ferrites. Results are consistent with a model in which Cr^{3+} substitutes into the B sites, has an even stronger B-site preference than Mn^{3+}, and displaces Co^{2+} ions onto A sites even more efficiently than Mn^{3+} does. Such characterizations and further measurements and analysis should help indicate how changes in Cr content affect thebulk magnetic and magnetoelastic properties of these materials, providing valuable information for future materials studies and applications of these materials.

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