Direct evidence for cobalt substitution effects in magnetite

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Abstract

We synthesized Fe 3 2xCo xO 4 x̂ 0 – 0.6 using the hydrothermal method in order to demonstrate substitutional effects on the hyperfine magnetic fields and populations of the tetrahedral (A) and octahedral (B) sites of magnetite. Our Mössbauer spectroscopy results provided direct evidence for the presence of the Co substitution in the B sublattice, which was found to be accompanied by a systematic increase of the hyperfine magnetic field at these sites. The mechanism we propose relies on the substitution of Fe 3+ by Co 2+ in the B sublattice and is supported by the observed dependence of the populations of the (A) and (B) sites on the content x of cobalt substitution. For the particular value x = 0.1, we report that the two sublattices of magnetite become equally populated. © 2000 Elsevier Science Ltd. All rights reserved.

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Magnetite (Fe3O4) is an oxide with the inverse spinel structure, which has one Fe 3+ ion on the tetrahedral (A) site and two Fe ions, with a total valence of 5+, on the octahedral (B) site [1,2]. Although the syntheses and transformations of various iron oxides and oxyhydroxides, such as hematite, maghemite and goethite have been studied in detail [3–11], not much is known about the formation of synthetic magnetites and the incorporation of impurity elements into them.

In the present paper we report the preparation of cobalt-doped magnetite by the hydrothermal method, in order to investigate the effect of cobalt substitution on the hyperfine magnetic fields and site populations in the magnetite structure. Fe 3–xCo xO 4 (x = 0–0.6) was prepared using the method of coprecipitation of the iron and cobalt hydroxides from sulphate solutions, mediated by sodium hydroxide in conditions controlled by concentration and pH (7.5). The reactive mixture was treated hydrothermally at 400°C for 30 min. Substituent concentrations in the resulting samples were determined using atomic absorption spectroscopy.

Room temperature transmission Mössbauer spectra were recorded using a constant acceleration spectrometer and a 57Co (Rh) source. The spectra were analyzed considering two sextets, corresponding to the tetrahedral (A) and octahedral (B) magnetic sublattices present in the samples. Least-squares fitting was performed using the NORMOS-SITE program and all variables of the fit were free. All Mössbauer spectra were fit with exactly the same set of initial parameters and the optimization results were clearly superior to those obtained with other fitting models: one sextet plus one field distribution or two field distributions. Selected transmission Mössbauer spectra are displayed in Fig 1(a)–(c), corresponding to a cobalt content x = 0, 0.3 and 0.6, respectively. It can be seen that increasing the amount x of cobalt substitution dramatically affects the B sublattice of magnetite, changing the shape of all transmission Mössbauer spectra. This demonstrates that Co ions exhibit a clear preference for the octahedral sites.

In order to quantify this effect, we extracted from these spectra the values of the hyperfine magnetic fields of the tetrahedral and octahedral sites and plotted them as functions of the amount x of cobalt substitution. Thus, it can be inferred from Fig. 2 that the hyperfine magnetic field of the tetrahedral sites is essentially not altered by the cobalt ions. This result is consistent with the fact that the cobalt impurities are not present at tetrahedral sites. In contrast to this, the hyperfine magnetic field of the octahedral sublattice increases steadily as a function of cobalt
concentration. This result demonstrates that the presence of cobalt at octahedral iron sites increases the values of the hyperfine magnetic fields at these positions. This behavior is similar to that observed in FeCoBSi metallic glass, which was found to exhibit an increased value of the hyperfine magnetic field at the iron sites, induced by the presence of cobalt atoms [12].

The mechanism by which Co$^{2+}$ substitutes for Fe$^{2+}$ in the B sublattice is supported by the concentration dependence of the populations of the tetrahedral and octahedral sites, derived from the areal ratios of the two sublattices in the Mössbauer spectra. In connection with Fig. 2, Fig. 3 provides direct evidence of this phenomenon: the population of the octahedral sites linearly decreases with increasing cobalt content, due to cobalt substituting iron. The population of the tetrahedral sites increases correspondingly.

It may be noted in Fig. 3 that there is a certain value of the
cobalt concentration ($x = 0.1$) for which the tetrahedral and the octahedral sublattices become equally populated. However, this result is influenced both by the number of cobalt ions and by the number of specific sites available in each sublattice.

To summarize, the main effects of the cobalt substitutions on the magnetic structure evidenced directly by our Mössbauer study are a linear increase in the hyperfine magnetic field and linear decrease in the population of the octahedral sublattice as functions of substituent concentration.

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References