A Mössbauer study of the Verwey transition in cobalt-doped magnetite

Monica Sorescu[a],*, A. Grabias[a,b], R.A. Brand[c], J. Voss[c], D. Tarabasanu-Mihaila[d], L. Diamandescu[d]

[a] *Bayer Center, Physics Department, Duquesne University, Pittsburgh, PA 15282-0321, USA*
[b] *Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland*
[c] *Gerhard Mercator Universitat, Duisburg, D 47048 Germany*
[d] *IFA, National Institute of Materials Physics, P.O. Box MG/7, Bucharest-Magurele, Romania*

Abstract

The low-temperature behavior of the Co-doped magnetite is studied. The $Fe_{3-x}Co_xO_4$ powders ($x = 0.01-1$) have been prepared by the hydrothermal method. In order to investigate the cobalt influence on the structure of magnetite, transmission Mössbauer spectroscopy measurements were performed at temperatures close and below the Verwey transition temperature characteristic for pure magnetite (122 and 77 K, respectively). All spectra were fitted with five components and related to nonequivalent Fe^{2+} and Fe^{3+} sites. The hyperfine parameters of these sites as well as their relative fractions in the powder samples were determined. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is known that pure magnetite undergoes a metal–insulator transition near 120 K. This the so-called Verwey transition is characterized by a large decrease in conductivity and a drop of the magnetization as well as by a heat capacity anomaly below the transition temperature [1]. Also, the crystal symmetry is lowered from cubic to monoclinic [2]. The Verwey transition is attributed to the charge ordering of Fe^{2+} and Fe^{3+} ions, however, the mechanism of ordering remains unclear. Mössbauer measurements of magnetite performed at temperatures below the Verwey transition temperature indicate the presence of five magnetic spectral components: one related to Fe^{3+} ions on the tetrahedral sites and four corresponding to Fe^{2+} and Fe^{3+} ions on two nonequivalent octahedral sites each [3].

The purpose of this work is to study the influence of the cobalt ions on the structure and magnetic properties of Co-doped magnetite powders at temperatures close and below the Verwey transition temperature. Transmission Mössbauer

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*Corresponding author. Tel.: +1-412-396-4166; fax: +1-412-396-4829.

E-mail address: sorescu@duq.edu (M. Sorescu).

spectroscopy is used to characterize the samples by determining the hyperfine parameters of the non-equivalent iron sites and their relative volume fractions. The low-temperature spectra allowed us to separate Fe^{2+} and Fe^{3+} ions on the octahedral sites and this was not possible in the case of room temperature spectra.

2. Experimental

Eleven compositions of the $Fe_{3-x}Co_xO_4$ powders with Co-content ranging from 0.01 to 1 have been prepared by the hydrothermal method [4]. Transmission Mössbauer spectroscopy measurements were performed at 122 and 77 K using a ^{57}Co-in-Rh source. Hyperfine parameters such as the hyperfine field, isomer shift, quadrupole shift and site populations have been determined using the NORMOS-SITE program.

3. Results and discussion

Mössbauer spectra of the selected $Fe_{3-x}Co_xO_4$ samples recorded at temperatures of 122 and 77 K are shown in Figs. 1 and 2, respectively. Our previous results of the room temperature Mössbauer spectra of the same $Fe_{3-x}Co_xO_4$ powders ($x = 0.01-1$), were fitted with two components: one corresponding to Fe^{3+} on the tetrahedral sites and the other one related to both Fe^{2+} and Fe^{3+} ions on the octahedral sites. They showed an increase in hyperfine magnetic field and a decrease in the population of the octahedral sites when Co content was increased [4]. This clearly indicates that Co^{2+} ions are preferably located on the octahedral sites of the inverse spinel structure. The introduction of Co substitution into the magnetite lattice causes a chemical disorder as a result of which the octahedral site components reveal broader spectral lines than the tetrahedral component [4–8].

Low-temperature spectra were fitted with five magnetic components (sextets): one corresponding to Fe^{3+} ions located on the tetrahedral sites and four related to Fe^{3+} and Fe^{2+} on the octahedral sites, in a similar way as in Ref. [3]. It has to be
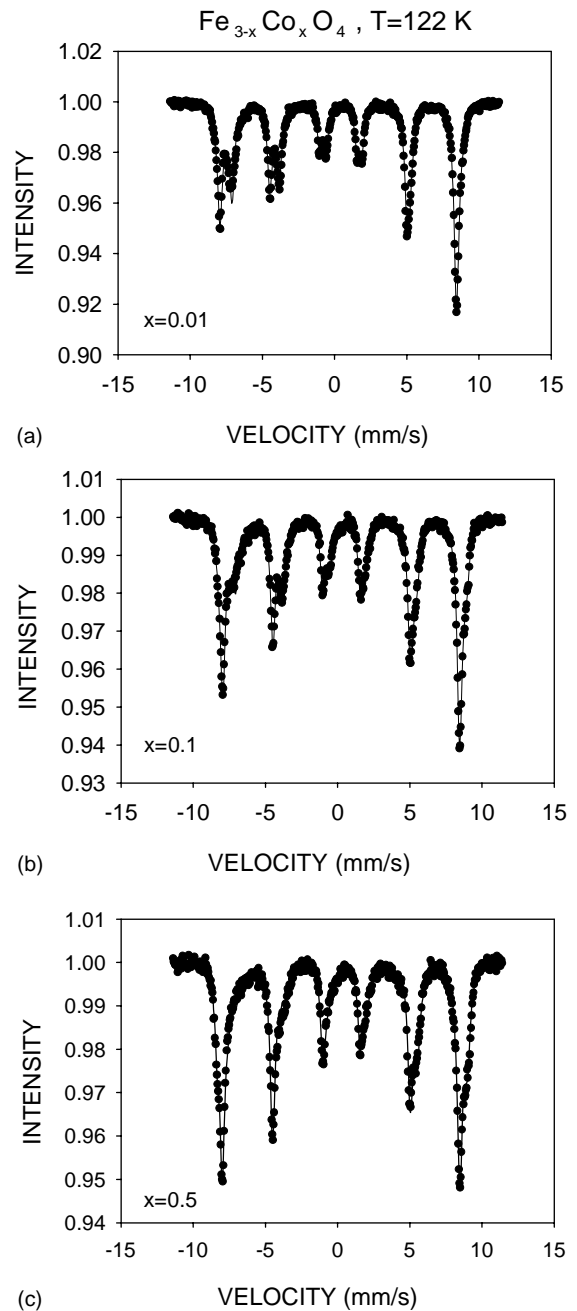

Fig. 1. Transmission Mössbauer spectra recorded at 122 K for cobalt-doped magnetite with (a) $x = 0.01$; (b) $x = 0.1$ and (c) $x = 0.5$.

mentioned that there is no agreement about the fitting method of the spectral components originating from the octahedral sites in the Co-doped
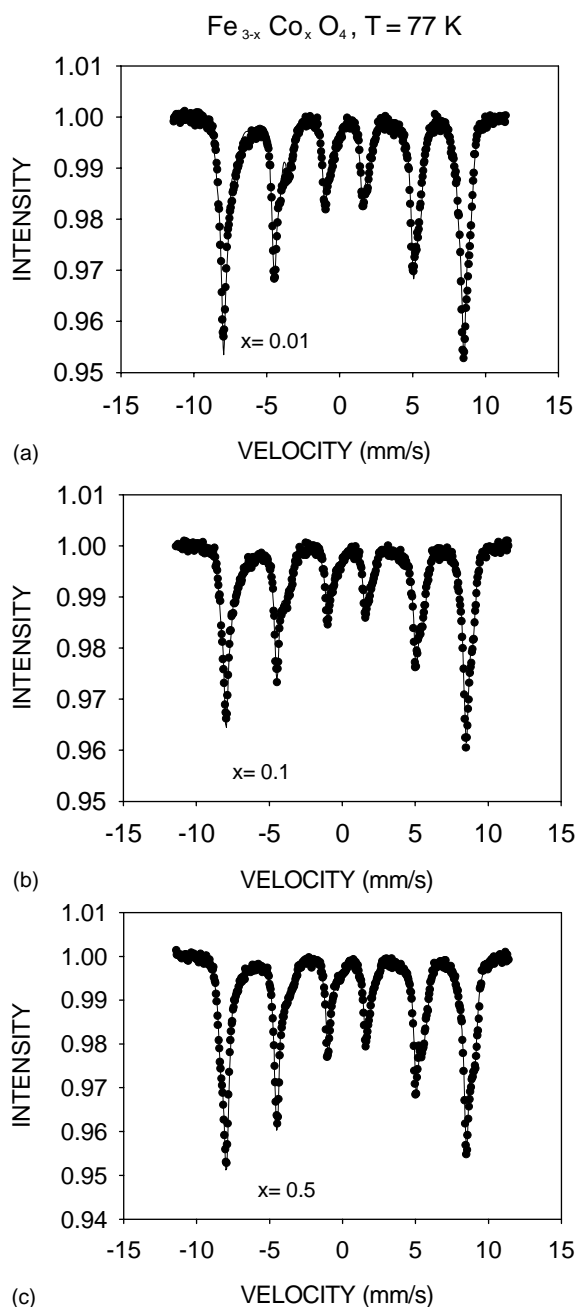
Fig. 2. Transmission Mössbauer spectra recorded at 77 K for cobalt-doped magnetite with (a) $x = 0.01$; (b) $x = 0.1$ and (c) $x = 0.5$.

magnetites [8,9]. Our low-temperature spectra clearly reveal at least three sextets beside the one related to the tetrahedral sites. The relative spectral contribution of the fourth sextet with the lowest hyperfine field is very small (2–3%). For the Fe_2CoO_4 ($x = 1$) sample the hyperfine fields extracted from the spectra measured at 122 K (Fig. 1) and 77 K (Fig. 2) are 50.9 T at 122 K (51.2 T at 77 K) for the tetrahedral sites, and 53.9 T (54.2 T), 50.4 T (50.9 T), 46.0 T (46.6 T) and 36.6 T (37.0 T) for the octahedral sites. The assignment of the sextets related to the octahedral sites is still controversial due to an electron-exchange process which involves nonlocalized 3d electrons and due to the broadening of the spectral lines resulted from the Co-induced chemical disorder. At low temperatures the states of iron ions in the octahedral sublattice seem to be strongly mixed so the notion of pure 2+ and 3+ valency may lose its meaning [8,10]. However, it can be assumed that the two highest hyperfine fields are related to the iron ions with valency close to 3+, whereas the other two correspond to Fe ions with valency close to 2+ [8]. In the real situation, the two magnetic components with the middle values of the hyperfine field originate from iron ions with valency somewhere in between 2+ and 3+. It was also concluded from the Mössbauer measurements of the $Fe_{3-x}Co_xO_4$ single crystals performed in an applied magnetic field [8] that the spectral component with the highest hyperfine field arises from iron which has a nominal charge in between 2.5+ and 3+ for $x = 0.1$ and then gradually evolves towards pure Fe^{3+} for $x = 1$. Therefore the different values of the hyperfine fields result from the different nearest-neighbor ionic configurations around the probe nuclei.

The dependence of the hyperfine fields on the cobalt content in the samples measured at 122 K is plotted in Fig. 3. There is a slight increase in the highest hyperfine field with increasing Co content, accompanied by a decrease of the hyperfine field of about 48–46 T. These trends are confirmed by the results obtained from the spectra measured at 77 K (Fig. 4). The highest hyperfine field increases from 53.3 T for $x = 0.01$ to 54.2 T for $x = 1$.

The site populations calculated from the spectra measured at 122 and 77 K are plotted versus cobalt content in Figs. 5 and 6, respectively. In both figures one can see the same trends. The population of the tetrahedral site increases slightly with
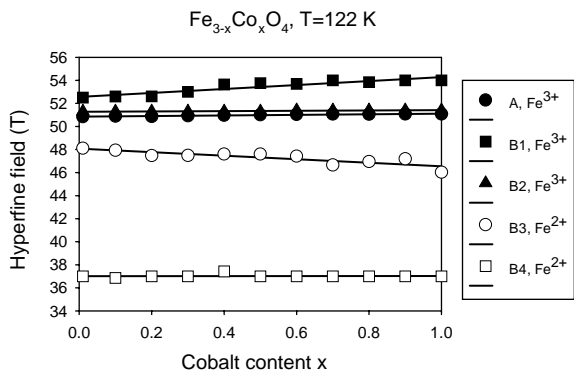
Fig. 3. Dependence of the hyperfine magnetic fields on the cobalt content x at the temperature of 122 K.
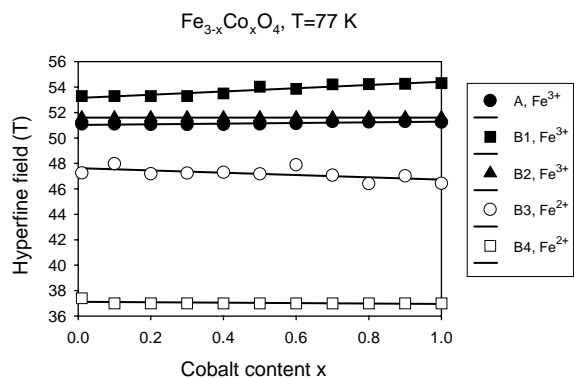

Fig. 4. Dependence of the hyperfine magnetic fields on the cobalt content at the temperature of 77 K.
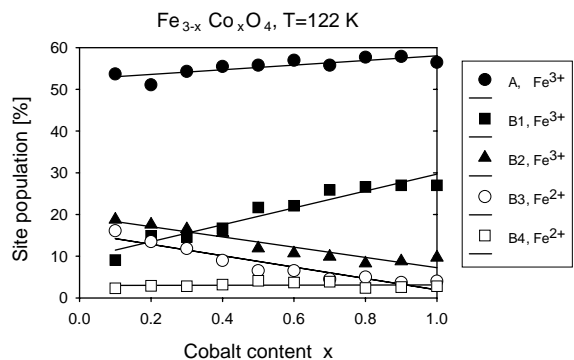

Fig. 5. Dependence of the site populations on the cobalt content x at 122 K.

the Co content. In the case of the octahedral sites, the populations of both Fe^{2+} sites decrease with increasing Co content and get close to 0 for $x = 1$.
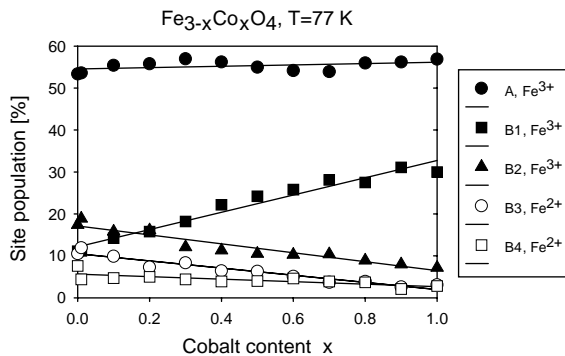

Fig. 6. Dependence of the site populations on the cobalt content x at 77 K.

This is because of the almost complete substitution of the Fe^{2+} ions by Co^{2+} for x close to 1. There is also a decrease in population observed for one of the Fe^{3+} sites with hyperfine field of about 50.8 T at 77 K and a very clear increase in the case of the Fe^{3+} site with the highest hyperfine field. Hence, for the Fe_2CoO_4 sample only two dominant magnetic components are observed: one corresponding to the tetrahedral sites and the other to the octahedral sites, both arising from the Fe^{3+} ions. From these results, one can conclude that the high-Co content in the doped magnetite powders prevents the charge ordering on the octahedral sites at low temperatures.

4. Conclusions

Eleven compositions of the hydrothermally prepared $Fe_{3-x}Co_xO_4$ powders with Co-content ranging from 0.01 to 1 have been studied by transmission Mössbauer spectroscopy at low temperatures. Co addition influences both the tetrahedral and octahedral sites in the doped magnetite. The hyperfine fields of all sites related to the Fe^{3+} ions increase slightly with increasing cobalt content, while for the Fe^{2+} components a slight decrease is observed. The populations of the Fe^{3+} and Fe^{2+} on the octahedral sites strongly depend on the cobalt content. Most apparent is the increase of the population of the Fe^{3+} ions on one of the octahedral sites with increasing Co content, which is correlated with the decrease observed for

other octahedral sites. It can be concluded from the site population results that the increase of Co addition decreases significantly the order–disorder transition temperature.

Acknowledgements

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