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Recoilless fraction of cobalt-doped magnetite

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ABSTRACT

Hydrothermally-synthesized $Fe_{3-x}Co_xO_4$ ($x = 0–0.9$) samples were analyzed by transmission Mössbauer spectroscopy in order to determine the recoilless fraction of the tetrahedral (A) and octahedral (B) sites as a function of the cobalt content x. Our 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 field at these sites. The recoilless fractions of the two sublattices were determined using our recently-developed dual absorber method. The recoilless fraction of the tetrahedral sites is practically constant, while that of the octahedral sites steadily decreases with increasing the Co content. These results tend to suggest that only the iron lattice participates in the recoilless process.

1. Introduction

The most important parameter in a Mössbauer effect experiment is the recoilless fraction $f = \exp(-k^2 < x^2 >)$, where k is the wave vector of the gamma ray and $< x^2 >$ is the mean square vibrational amplitude of the resonant atom in the direction of observation. The main method available to date for the determination of the recoilless fraction relies on the temperature dependence and the determination of the Debye temperature from complicated equation plots, with errors often recognized to be significant [1–23]. However, we have recently proposed a new method [24] for the direct determination of the recoilless fraction using a single room-temperature transmission Mössbauer measurement. The method relies on a two-absorber comparative approach and made it possible to determine the recoilless fraction of various systems, from iron chlorides to nanoparticles [25–32]. Most recently, our approach was favorably cited in [33], as a way around the subtle background problem, which offers a very attractive, accurate and extremely simple method to determine the recoilless fraction.

Magnetite (Fe_3O_4) 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. In this paper we synthesized cobalt-doped magnetite powders of the form $Fe_{3-x}Co_xO_4$ ($x = 0–0.9$) in order to perform a Mössbauer spectroscopy study of the substitutional effects on the hyperfine magnetic fields and recoilless fraction of both tetrahedral and octahedral sublattices.

2. Experimental

$Fe_{3-x}Co_xO_4$ ($x = 0–0.9$) was prepared hydrothermally using the method of coprecipitation of the iron and cobalt hydroxides from sulfate solutions [34], mediated by sodium hydroxide in conditions controlled by concentration and pH (7.5). The reaction mixture was treated hydrothermally at 300 °C for 30 min.

Room temperature transmission Mössbauer spectra were recorded using a constant acceleration spectrometer and a ^{57}Co (Rh) source of 10 mCi. Least-squares fitting was performed using the NORMOS-SITE program. All variables of the fit were free and all spectra were fitted with exactly the same set of initial parameters.

All our samples were less than 20 μm in thickness, such that the thin absorber approximation could be used, without the need of introducing transmission integrals. The use of different lineshapes would be possible as a further refinement of our model. Moreover, in Ref. [24] we provided an experimental demonstration of the absence of thickness effects in our model, using interchanged and split area absorbers.

3. Results and discussion

Fig. 1(a) shows the room temperature transmission Mössbauer spectrum of pure magnetite. The spectrum was analyzed using two sextets, corresponding to the tetrahedral (A) and octahedral (B) magnetic sublattices. Fig. 1(b) represents the composed

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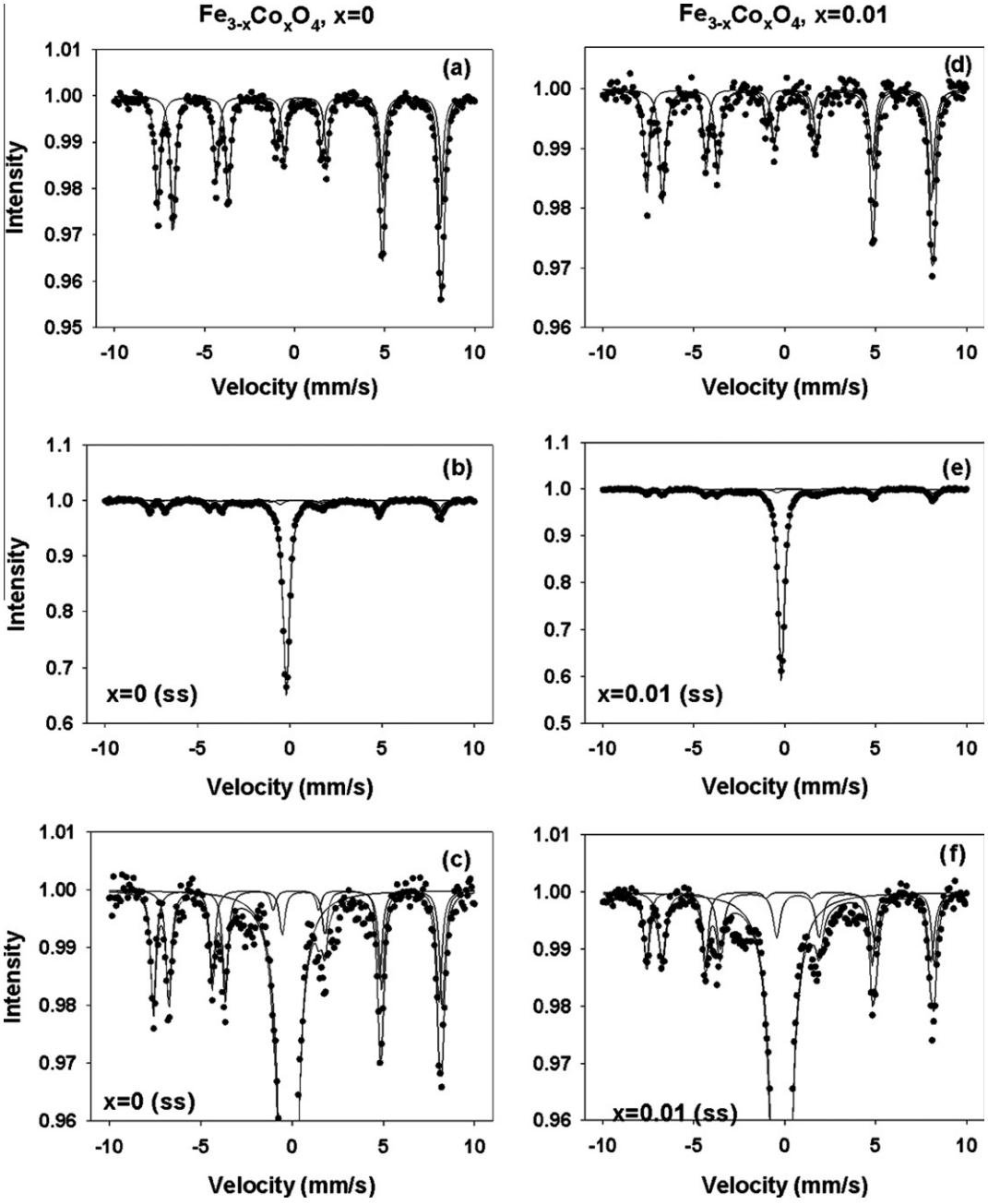

Fig. 1. (a) Room temperature transmission Mössbauer spectrum of magnetite, (b) magnetite with stainless steel (SS) absorber, (c) magnification of the spectrum in (b), (d) room temperature transmission Mössbauer spectrum of cobalt-doped magnetite at $x = 0.01$, (e) cobalt-doped magnetite ($x = 0.01$) with SS and (f) magnification of the spectrum in (e).

Mössbauer spectrum of the magnetite and the stainless steel (SS) foil. This method relies on the simultaneous recording of the Mössbauer spectrum for a sandwich of two absorbers, out of which one (the SS foil) has a known value of the recoilless fraction ($f_s = 0.7$). The recoilless fraction of the absorber under investigation is then determined from the area ratios of the subspectra and some chemical arguments [24]. Since its development, our dual-absorber method has been successfully used to determine the recoilless fraction of iron oxide nanoparticles [25,28], tin-doped hematite nanoparticles [26], iron chlorides [27], zirconium-doped hematite nanoparticles [29], cerium-doped hematite nanoparticles [30], mechanochemically-synthesized hematite nanoparticles [32] as well as to demonstrate the enhancement of the recoilless fraction in intermetallic compounds after hydrogenation [31]. Most recently, our method has been adopted to study the recoilless fraction of the stainless steel as affected by applying different line shape approximations [33]. The method was judged by this author as a very attractive and extremely simple way and found to work satisfactorily for the investigated absorbers.

Fig. 1(c) displays a magnification of the spectrum in Fig. 1(b). It can be seen that the spectrum was fitted with two sextets, corresponding to the tetrahedral and octahedral sites of magnetite, plus a single resonance representing the pattern of the SS. Following the