

Mössbauer effect of Ni-doped strontium ferrite

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Abstract We applied ^{57}Fe Mössbauer spectroscopy to determine occupation sites of Ni atoms in the hexagonal M-type strontium ferrite. From spectral analyses of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{11.6-x}\text{Ni}_x\text{O}_{19}$ with $x \leq 0.35$ at room temperature, we propose that Ni atoms occupy preferentially octahedral Fe ($12k$, $4f_2$ and $2a$) sites.

Keywords M-type hexagonal ferrite · Mössbauer effect · Site assignment

1 Introduction

The hexagonal magnetoplumbite-type (M-type) strontium ferrite is widely used as a permanent magnet owing to its excellent cost performance and high chemical stability. Thus, the improvement in its magnetic performance makes great impact on various fields. In $\text{SrFe}_{12}\text{O}_{19}$, the substitution of the transition-metal element Co is known to improve performance as a hard magnet [1, 2]. Since the Fe sublattice consists of five crystallographic sites (octahedral $12k$, $4f_2$, $2a$, tetrahedral $4f_1$, and bipyramidal $2b$), it is important to assign the sites occupied preferentially by Co atoms to know the function of Co and further to develop new advanced magnets in the next generation. For the sake, we have employed the Mössbauer measurements to confirm the Co occupation sites in $(\text{Sr}^{2+}\text{-La}^{3+})(\text{Fe}^{3+}\text{-Co}^{2+})_{12}\text{O}_{19}$, and obtained experimental results (Akasaka et al. unpublished manuscript) being thoroughly consistent with previous ones such as in [3], indicating that Co atoms occupy preferentially octahedral $4f_2$ (and possibly $2a$) site(s). This has been supported by Raman

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spectroscopy [4]. However, this argument was found to be in discordance with the conclusion obtained recently from simultaneous analyses of neutron diffraction and extended X-ray absorption fine structure (EXAFS) spectra, which excludes $4f_2$ and $2b$ sites as possible Co occupation sites [5]. Furthermore, in previous studies, Co occupation at the $4f_1$ site has actually been suggested from neutron diffraction [6] and NMR measurements [3]. X-ray magnetic circular dichroism (XMCD) measurements also indicated that Fe atoms at the $4f_1$ site are replaced by Co [5]. This discrepancy may originate in the site assignment in Mössbauer analyses, for example, incorrect assignment between $4f_1$ and $4f_2$ sites with the same atomic fraction. However, a recent first-principle calculation (Ikeno and Tanaka, private communication) showed that sequences of calculated hyperfine parameters at the five different sites are completely consistent with the previous experimental assignment [7], excluding such a possibility of the incorrect assignment. Thus, as another approach to find out the origin of this discrepancy, we plan to check the consistency between Mössbauer and other experimental methods by measuring another system substituted by a different transition metal element. Here, we report a part of the study, Mössbauer results of Ni-doped strontium ferrites.

2 Experimental procedures

A series of powder samples were synthesized by solid state reaction by using powder materials SrCO_3 , $\text{La}(\text{OH})_3$, NiO , and Fe_2O_3 . The raw materials were weighed in the nominal ratio in a chemical formula $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{11.6-x}\text{Ni}_x\text{O}_{19}$ ($x \leq 0.35$), mixed with a ball mill in water, dried at 432 K for 24 h in air, and calcined at 1523 K for 20 h in air. ^{57}Fe Mössbauer spectra were recorded with a conventional constant-acceleration-type spectrometer using a $^{57}\text{Co}(\text{Rh})$ source at room temperature.

3 Results and discussion

Figure 1 shows the Mössbauer spectrum of $\text{Sr}_{0.8}\text{La}_{0.2}\text{Fe}_{11.4}\text{Ni}_{0.2}\text{O}_{19}$ at room temperature, as an example of experimental spectra. The spectrum was fitted assuming the presence of five different Fe sites. As a first step, possible emergence of Fe^{2+} atoms at the $2a$ site [8] was neglected. One may see relatively large discordance at some minor peaks, which is mainly ascribed to this simplification. In fact, the information only at room temperature may not be sufficient in this kind of analysis with a lot of fitting parameters. In the present case, we relied on the previous comprehensive analysis for the non-doped sample [3], used predetermined hyperfine parameters as initial values for the fitting, and confirmed that this method works well to discuss the Co occupation site in the Co-doped system.

Hyperfine parameters (isomer shift, quadrupole split and hyperfine field) obtained in the analysis are plotted against the Ni concentration, x , in Fig. 2. Concentration dependences of the parameters are not marked, and general trends are in agreement with those of Co-doped system (Akasaka et al. unpublished manuscript). Occupation ratios of Fe atoms for the Ni-doped system, which were estimated from integrated spectral intensities, are plotted in Fig. 3. Here we fixed the ratio of the $4f_1$ site to a constant value, four, because preliminary free-parameter fitting clearly

Fig. 1 Mössbauer spectrum of $\text{Sr}_{0.8}\text{La}_{0.2}\text{Fe}_{11.4}\text{Ni}_{0.2}\text{O}_{19}$ at room temperature fitted assuming the presence of five different Fe sites (red: 12k, blue: $4f_2$, yellow: $4f_1$, green: 2a, purple: 2b)

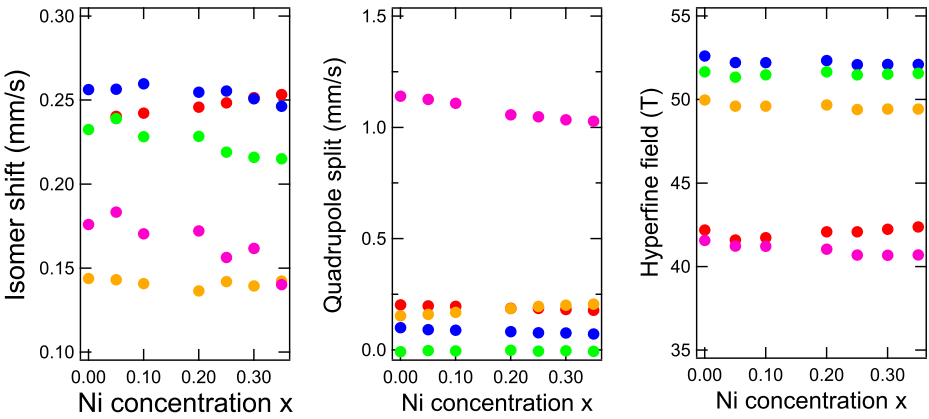
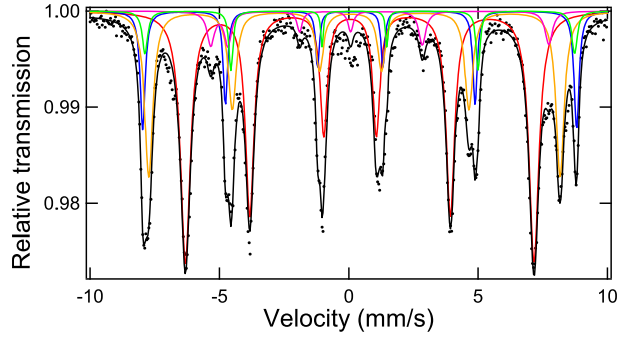
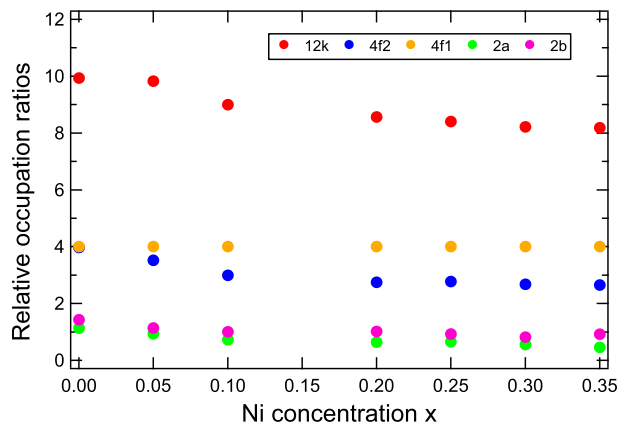


Fig. 2 Hyperfine parameters of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{11.6-x}\text{Ni}_x\text{O}_{19}$ at room temperature plotted against the Ni concentration, x . See Fig. 1 for the symbol color

Fig. 3 Relative occupation ratios of Fe atoms in $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{11.6-x}\text{Ni}_x\text{O}_{19}$ plotted against the Ni concentration, x . The ratio of the $4f_1$ site was fixed to four



indicated that it does not decrease with x . Thus, relative values with respect to four for the $4f_1$ site are plotted for the other sites in the figure. The intensity ratio of $12k$, $4f_1$, $4f_2$, $2a$ and $2b$ for the non-doped sample is not $12 : 4 : 4 : 2 : 2$, which is possibly ascribed to the anisotropic Debye-Waller factor depending on the site and/or the presence of some defects in the compounds. As seen in the figure, the intensities of $12k$, $4f_2$ (and possibly $2a$) sites decrease appreciably with the Ni substitution, suggesting Ni atoms occupy nearly randomly the octahedral sites.

In conclusion, Mössbauer experiments suggest that Ni atoms occupy octahedral $12k$, $4f_2$ (and possibly $2a$) sites in Ni-substituted M-type ferrites, $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{11.6-x}\text{Ni}_x\text{O}_{19}$ ($x \leq 0.35$). We are planning to make other experiments such as neutron diffraction and X-ray absorption fine structure measurements in order to cross-check with the present Mössbauer result and elucidate the origin of the discrepancy in the Co-doped sites.

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