ELSEVIER

Journal of Magnetism and Magnetic Materials 232 (2001) 175–180

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Mössbauer characterization of $Nd_{0.7}Sr_{0.3}(Mn_{1-x}{}^{57}Fe_x)O_3$ ($x = 0.02$–0.15)

H.H. Hamdeh[a], J.C. Ho[a,]*, S.A. Oliver[b], J.G. Lin[c], S.Y. Lin[c], P.C. Kuo[c], C.Y. Huang[c]

[a] *Department of Physics, Wichita State University, Wichita, KS 67260-0032, USA*
[b] *Center for Electromagnetic Research, Northeastern University, Boston, MA 02115, USA*
[c] *Center for Condensed Matter Sciences and Engineering, National Taiwan University, Taipei, Taiwan*

Received 13 December 2000; received in revised form 9 March 2001

Abstract

The magnetic structure of colossal magneto-resistive $Nd_{0.7}Sr_{0.3}(Mn_{1-x}{}^{57}Fe_x)O_3$ ($x = 0.02$, 0.05, 0.10, and 0.15) has been studied by Mössbauer spectroscopy in magnetic fields up to 60 kG. ^{57}Fe ions appear to spread over two different magnetic phases. One of them remains ferromagnetic for all values of x, but the other one changes from canted to antiferromagnetic with increasing x. For $x = 0.02$ and 0.05, the latter magnetic phase is comprised of small clusters, which are very sensitive temperature and strongly influenced by the applied fields. © 2001 Published by Elsevier Science B.V.

PACS: 75.30.Vn; 75.25.+z; 76.80.+y

Keywords: CMR material; High field Mössbauer

---

1. Introduction

Numerous studies have been conducted on perovskite compounds having the composition $R_{1-y}M_yMnO_3$ (R = trivalent lanthanide; M = divalent element) since the initial realization of their colossal magnetoresistance [1,2]. Most of these efforts have focused on optimizing and explaining the greatly enhanced magnetotransport properties by systematically varying the Mn^{3+}/Mn^{4+} ratio in the material through modifications of the divalent cation concentration within the perovskite structure [3]. Less effort has been spent in examining the effects of substitutions on the octahedral sites occupied by the manganese cations, in part because such a replacement causes a quenching of the desirable magnetotransport properties [4]. However, a systematic examination of the changes in micromagnetic properties of the perovskites with cation substitution for manganese can reveal insight on the dependence of the local spin moment behavior on cation occupation and the competition between exchange mechanisms for manganese cations having different nearest-neighbor combinations.

Such information on the local spin moment behavior may be obtained by straightforwardly replacing Mn^{3+} cations by Fe^{3+} cations within

---

*Corresponding author. Tel.: +1-316-978-3992; fax: +1-316-978-6556.

E-mail addresses: jchohoho@hotmail.com (J.C. Ho).

PII: S0304-8853(01)00203-7

the perovskite structure. Here, both manganese and ferric iron ions have similar ionic radii while occupying octahedral sites [5] such that this substitution is expected to minimally impact the lattice parameters, although it has been noted that this substitution may change the Mn–O–Mn bond angles and thus modify the exchange interactions [6]. Most importantly, the substitution of $^{57}Fe^{3+}$ for Mn^{3+} allows inference of the behavior of the majority manganese spin system through the usage of Mössbauer effect measurements. Unfortunately, the behavior of the Fe^{3+} spin moments in these manganites will not necessarily reproduce those of the Mn^{3+}, since the iron cations always have an antiferromagnetic exchange coupling to magnetic ions on neighboring sites through the superexchange interaction, whereas the manganese cations can have either an antiferromagnetic or ferromagnetic exchange coupling to nearest-neighbor manganese cations depending upon the respective types and valencies of the involved cations. Thus, small replacements of iron for manganese can be viewed as a perturbation of the magnetic ground state, whereas very large substitutions are expected to drive the spin system towards an antiferromagnetic state exemplified by the orthoferrite compound $LaFeO_3$. Meanwhile, intermediate levels of substitution are expected to inject a considerable amount of frustration into the spin system since the manganese cations will have competing couplings by both the antiferromagnetic superexchange and ferromagnetic double-exchange interaction to neighboring magnetic ions.

In this work, we have examined the micromagnetic response of the spin system in the perovskite compound $Nd_{0.7}Sr_{0.3}(Mn_{1-x}{}^{57}Fe_x)O_3$ ($x = 0.02$–0.15) through the usage of Mössbauer effect measurements at temperatures down to 4.2 K and applied fields up to 60 kG. This study follows previous measurements of the magnetic and magnetotransport properties of this system [7]. The macroscopic magnetic properties evolve from those typical of the ferromagnetic perovskites that show a colossal magnetoresi stance effect for $x = 0$, to a material that shows antiferromagnetic ordering and canted behavior for an iron substitution of $x = 0.15$. This evidence for strong competition between exchange couplings at moderate levels of iron substitution has been extended to single crystal materials of pure $Nd_{0.7}Sr_{0.3}MnO_3$, where recent ac-susceptibility measurements have been interpreted as indicating that a significant competition between antiferromagnetic and ferromagnetic exchange mechanisms exists even in the ferromagnetic phase of these unsubstituted crystals [8]. Thus, it is evident that the $Nd_{0.7}Sr_{0.3}(Mn_{1-x}{}^{57}Fe_x)O_3$ system possesses intriguing spin moment behaviors even to the lowest substitution levels.

2. Experimental Procedure

The pressed powder $Nd_{0.7}Sr_{0.3}(Mn_{1-x}{}^{57}Fe_x)O_3$ ($x = 0.02$, 0.05, 0.10, and 0.15) samples were produced by the solid state synthesis process given in Ref. [7]. To allow for high quality Mössbauer effect measurements, pure $^{57}Fe_2O_3$ was used in stoichiometric proportions with Nd_2O_3, $SrCO_3$, and $MnCO_3$. The mixture was milled and calcined at 1200°C in air for 16 h, milled again and pressed into a pellet under a 3-ton/cm^2 pressure, and then given a final sintering at 1400°C for 16 h. Room temperature X-ray diffraction on powder samples showed only peaks corresponding to the orthorhombic perovskite-like structure, with no significant change in lattice parameters occurring with iron substitution. One expected result of this Fe^{3+} cation substitution for Mn^{3+} is a shift in balance between Mn cations having differing valence states. In particular, the predicted Mn^{3+}/Mn^{4+} ratio of $(0.7 - x)/0.3$ will vary from 2.33 for $x = 0$–1.83 and for $x = 0.15$, as is shown in Fig. 1.

Mössbauer measurements were taken in the transmission mode, with two ^{57}Co sources mounted on the ends of the shaft in a standard constant acceleration drive unit. The first, 70 mCi ^{57}Co, source was used to measure the absorption lines of the samples under study, while the second, 25 mCi ^{57}Co, source was used to calibrate the drive unit with pure Fe for every measurement in order to eliminate the effects of stray magnetic fields. Each powder sample was prepared between two layers of thin tape, and was then mounted on the finger of a liquid ^4He-flow cryostat. The sample

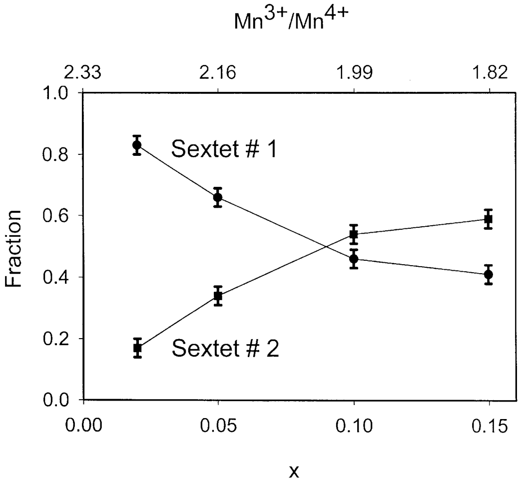

Fig. 1. Varying abundance of the two sextets with respect to Fe concentration and the corresponding Mn^{3+}/Mn^{4+} ratio.

assembly was then placed in the bore of a superconducting solenoid magnet, such that the gamma ray beam was directed along the magnetic field axis for all measurements.

3. Results and discussion

All samples showed the distinct ^{57}Fe hyperfine sextet patterns in the Mössbauer spectra expected for long range magnetic ordering at temperatures below 20 K. An inspection of the Mössbauer data taken at zero applied field indicated that each spectra is best fitted by a pair of sextets having different hyperfine field parameters and line widths. The hyperfine parameters extracted from the zero field data are listed in Table 1, along with the line widths. These results show that the mean hyperfine magnetic field (HMF) of both sextets decreases with increasing Fe concentration. Moreover, both sextets were found to be very sensitive to temperature between 10 and 20 K, with the sextet of lower HMF showing the greater decrease in HMF. Thus, the two sextets will be denoted in terms of the respective values of their hyperfine magnetic fields, such that the "first sextet" always showed the larger HMF in each measurement. The isomer shift of the both sextets (0.35–0.40 mm/s; relative to pure Fe) were typical of Fe^{3+} in an octahedral coordination [9], indicating a straightforward substitution of Fe^{3+} for Mn^{3+} within the lattice as x increases, as expected for the similar ionic radii of the Mn^{3+} and Fe^{3+} cations. Values for the population of each sextet were found from the sextet relative area, and are shown in Fig. 1. Here the increase in population of the second sextet with x is clearly apparent.

The major finding of this Mössbauer study is undoubtedly the existence of the second sextet, which has not been reported by previous studies on similar CMR materials with $x = 0.02$ [10,11], perhaps due to its shallowness and great sensitivity to temperature. The presence of this feature may have been obscured from previous measurements because it may have been buried underneath the first (high intensity) sextet at 4.2 K, while at higher temperatures it may be smeared due to broadening of the linewidth caused by fast relaxation processes, as will be described below.

Due to the sensitivity of the spin ordering in these perovskites to applied magnetic fields, the micromagnetic behavior of the $^{57}Fe^{3+}$ cations was further investigated by taking the Mössbauer effect

Table 1
Zero-Field Mössbauer data fitting parameters representing two sextets for each Fe content

Sample (x)	Temperature (K)	HMF_1 (kG)	HMF_2 (kG) (mm/s)	Line $width_1$ outer line (mm/s)	Line $width_2$ outer line (mm/s)
0.02	10	540	484	0.41	1.16
	17	514	440	0.50	1.21
0.05	16	515	458	0.53	1.04
0.10	15	477	444	0.58	1.25
0.15	15	477	440	0.59	0.90

measurements at applied fields up to 60 kG at a fixed temperature of 10 K. For the measurement geometry used here, the spin state of each sextet can be appraised by the behavior of the second and fifth lines of the sextet upon application of a strong longitudinally oriented magnetic field (*H*). In particular, the intensity of the second and fifth lines will vanish if the spins are oriented either in a ferromagnetic or ferrimagnetic state. In contrast, it will be unaffected by *H* if the system has antiferromagnetic ordering, but will decrease gradually with *H* if the spins exist in a disordered or spin glass state.

Mössbauer spectra taken at high magnetic fields are shown for the different samples in Figs. 2–5. These figures also show the fitting results, which represent the summation of the two hyperfine sextets. Qualitatively, the first sextet behaves similarly for each sample at the same *H* value. The second and fifth lines of this sextet disappear around 20 kG and the HMF increases linearly with the applied field, as shown in Fig. 6. This behavior shows that the $^{57}Fe^{3+}$ spins of the first sextet are ferromagnetically ordered, and are aligned antiparallel to the applied field. In turn, this implies that the Mn majority spins have ordered ferromagnetically and are aligned parallel to the applied field, since the iron spins are coupled anti ferromagnetically to them through the superexchange interaction.

In contrast to the first sextet, the second (lower HMF) sextet goes through a more complex evolution with increasing $^{57}Fe^{3+}$ substitution. A marked drop is noted in the HMF of this sextet for the $x = 0.02$ and 0.05 samples above 20 and 30 kG, respectively, as shown in Fig. 6. These drops are associated with a rapid decrease in the intensity of the second and fifth lines of each sextet, which disappear completely at 40 and 50 kG for $x = 0.02$ and 0.05, respectively, as shown in Fig. 7. The intensity ratio in Fig. 7 is the ratio of the area under the second and fifth lines to the area under

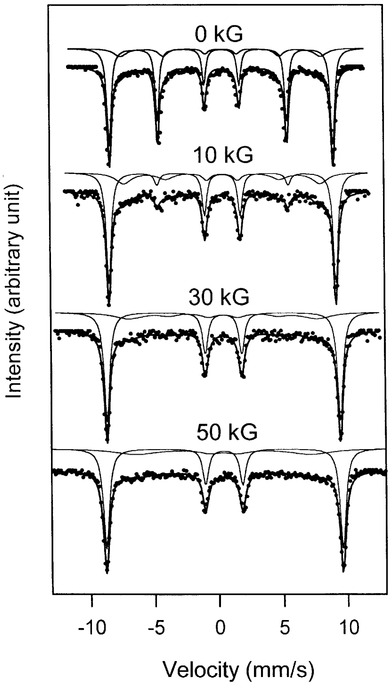

Fig. 2. Mössbauer spectra for $x = 0.02$ at 10 K in the indicated external fields. The solid lines are the calculated sextets and their sum.

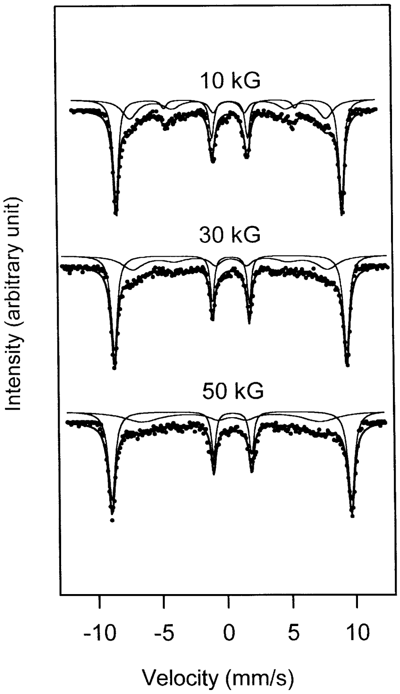

Fig. 3. Mössbauer spectra for $x = 0.05$ at 10 K in the indicated external fields. The solid lines are the calculated sextets and their sum.

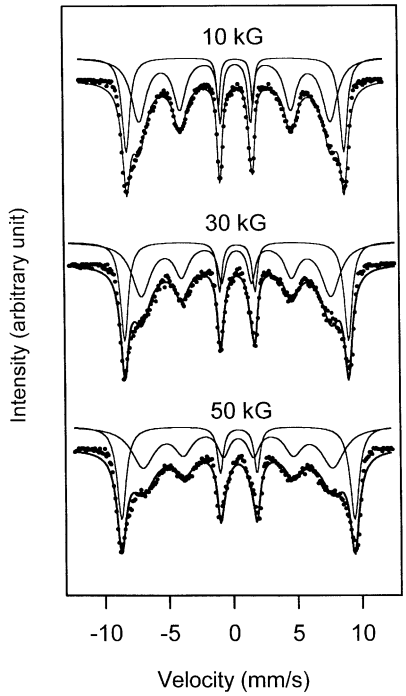

Fig. 4. Mössbauer spectra for $x = 0.10$ at 10 K in the indicated external fields. The solid lines are the calculated sextets and their sum.

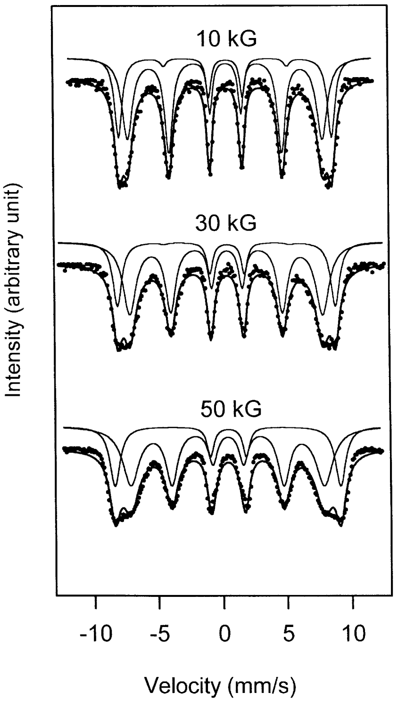

Fig. 5. Mössbauer spectra for $x = 0.15$ at 10 K in the indicated external fields. The solid lines are the calculated sextets and their sum.

the first and sixth lines. At lower fields, the decrease in HMF and the intensity of the second and fifth lines are typical of Fe moments gradually rotating into the direction of the applied fields. However, this interpretation must be coupled with the remarkable broadening of the remaining lines of the sextet at high fields.

One mechanism that can explain this overall behavior is the dominance of fast magnetic relaxation processes at fields higher than 20 kG for $x = 0.02$, and 30 kG for $x = 0.05$. Seemingly, the second sextet originates from Fe ions occupying magnetic clusters with canted order. These clusters are small enough for the applied fields to reduce the energy barrier and cause rapid fluctuations of the transverse component of the Fe moments. Then the net average of the transverse component of the HMF decreases to zero as the fluctuations become faster than the Mössbauer measurement time (of the order of 10^{-8} s) as the applied field increases [12]. The consequences of this behavior include both the rapid drop of the HMF and the vanishing of intensity for the second and fifth lines. It is also worth noting that this information on the micromagnetic behavior will be undetectable by magnetization measurements, since the magnitude of the measured magnetization is unaffected regardless of whether the transverse components of the spin moments are frozen randomly or fluctuating.

In contrast to the samples having small x, the Mössbauer effect results for samples having a substantial iron substitution show behaviors attributable to antiferromagnetic ordering. For the $x = 0.1$ sample, the intensity of the second and fifth lines of the sextet does not vanish even at 60 kG (Figs. 4 and 6) indicating non-collinear spin ordering. However, the HMF shown in Fig. 7 does show a gradual decrease for H less than 40 kG before leveling off at higher fields. Both of

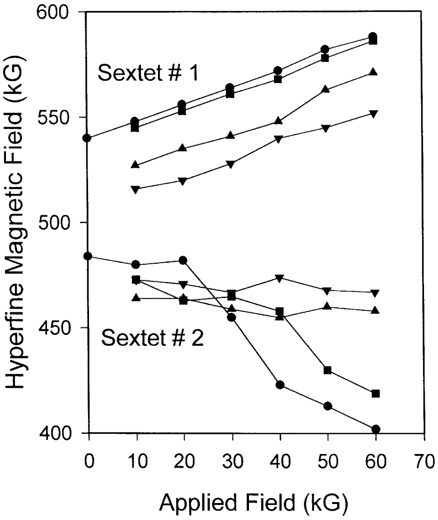

Fig. 6. Field dependence of the hyperfine magnetic fields of the two sextets at 10 K.

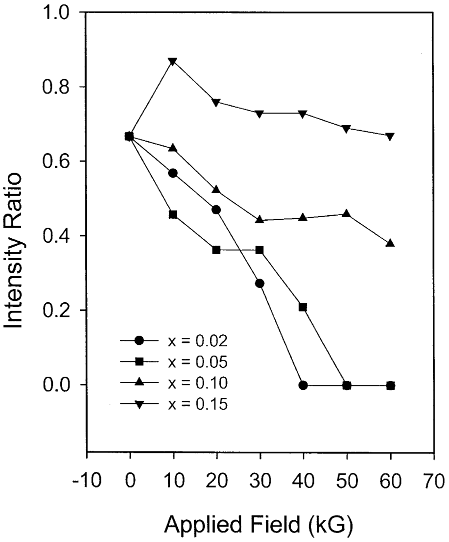

Fig. 7. Field dependence of the relative intensity ratio of the second and fifth lines of the second sextet at 10 K.

these observations imply that the net spin state has at least a partial antiferromagnetic ordering. The evolution of this sextet into one showing true antiferromagnetic ordering occurs for $x=0.15$ sample, as demonstrated by the insensitivity of both the HMF and the intensity of the second and fifth lines to the applied fields, as shown in Figs. 6 and 7.

4. Conclusions

Based on the Mössbauer spectroscopic data, trivalent Fe ions in $Nd_{0.7}Sr_{0.3}(Mn_{1-x}{}^{57}Fe_x)O_3$ reduce the Mn^{3+}/Mn^{4+} ratio. Moreover, the second and new magnetic phase is identified in the colossal magnetoresistive materials. For $x=0.02$ and 0.05, this phase is composed of small clusters, which are highly sensitive to both temperature and magnetic fields. Their magnetic behavior could conceivably contribute to the transport properties.

References

[1] R. von Helmolt, J. Weeker, B. Holzapfel, L. Schultz, K. Samwer, Phys. Rev. Lett. 71 (1994) 2331.
[2] M. McCormick, S. Jin, T.H. Tiefel, R.M. Fleming, J.M. Phillips, R. Ramesh, Appl. Phys. Lett. 64 (1994) 3045.
[3] For an excellent review, see J.M.D. Coey, M. Viret, S. von Molnár, Adv. Phys. 48, (1999) 167 and references therein.
[4] K.H. Ahn, X.W. Wu, K. Liu, C.L. Chien, J. Appl. Phys. 81 (1997) 5505.
[5] S. Krupicka, P. Novak, in: E.P. Wohlfarth, (Ed.) Ferromagnetic Materials, Vol. 3, North-Holland Publ. Co., Amsterdam, 1982, p. 189.
[6] L. Righi, P. Gorria, M. Insausti, J. Gutiérrez, J.M. Barandiarán, J. Appl. Phys. 81 (1997) 5767.
[7] S.Y. Lin, J.G. Lin, P.C. Kuo, C.Y. Huang, Proceedings of the 14th Conference on Magnetism and Magnetic Technologies, Taiwan, 2000, p. 69.
[8] J.-G. Park, M.S. Kim, H.-C. Ri, K.H. Kim, T.W. Noh, S.-W. Cheong, Phys. Rev. B 60 (1999) 14804.
[9] P.A. Dickof, P.J. Schurer, A.H. Morrish, Phys. Rev. B 22 (1980) 115.
[10] A. Tkachuk, K. Rogacki, D.E. Brown, B. Dabrowski, A.J. Fedro, C.W. Kimball, B. Pyles, X. Xiong, Daniel Rosenmann, B.D. Dunlap, Phys. Rev B 57 (1998) 8509.
[11] M. Pissas, G. Kallias, E. Devlin, A. Simopoulos, D. Niarchos, J. Appl. Phys. 81 (1997) 5770.
[12] S. Mørup, Hyperfine Interactions 60 (1990) 959.