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A ^{57}Fe Mössbauer study of charge ordering and phase separation in the rare-earth manganates, $Nd_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$

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Abstract

Mössbauer studies of 2% ^{57}Fe-doped $Nd_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$ have been carried out over the 4.2–300 K range after ensuring that such doping does not change their basic properties. The charge-ordering transition in these manganates is marked by abrupt changes in the quadrupole splitting. In the case of $Nd_{0.5}Ca_{0.5}MnO_3$, two phases manifest themselves on cooling below the charge-ordering transition temperature. The evolution of the spectra as a function of temperature shows that long-range magnetic order does not occur sharply. The observed evolution with temperature is different in the two materials studied. In $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$, it resembles that of a disordered magnetic material, whereas the temperature dependence of line shape of $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ is typical of a superparamagnetically relaxed magnetic system. Although both the manganates show well-resolved magnetic hyperfine spectra at 4.2 K, the lines are slightly broad indicating possible coexistence of phases at low temperatures. A weak paramagnetic signal is also seen in the spectra of both the manganates at 4.2 K.
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1. Introduction

Charge ordering in rare-earth manganates of the type $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = alkaline earth) has been investigated widely [1, 2]. Many of these manganates also show effects of phase separation [3, 4]. We wanted to investigate the typical scenario of charge ordering, magnetic ordering and phase separation in the rare-earth manganates by Mössbauer spectroscopy, which is a local probe. For this purpose, we have chosen two compositions with distinctly different charge-ordering behaviors, namely $Nd_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$. In $Nd_{0.5}Ca_{0.5}MnO_3$, charge ordering occurs in the paramagnetic phase at 240 K followed by a transition to a canted antiferromagnetic (AFM) state on cooling to low temperatures [5]. The presence of ferromagnetic correlations at low temperatures has also been observed in this compound [6]. $Nd_{0.5}Sr_{0.5}MnO_3$, on the other hand becomes ferromagnetic around 250 K

and undergoes a transition to the charge-ordered CE-type AFM state on cooling to 150 K [7]. $Nd_{0.5}Sr_{0.5}MnO_3$ is also shown to undergo a transition to A-type AFM state on cooling the ferromagnetic state below 225 K followed by the transition to a CE-type AFM state below 150 K. At very low temperature, all the three phases are reported to coexist in some samples of $Nd_{0.5}Sr_{0.5}MnO_3$ [8, 9]. After ensuring that the small doping (2%) of ^{57}Fe at the Mn site of these two manganates does not change the structure or the phase transition significantly, we have carried out ^{57}Fe Mössbauer studies as a function of temperature from 300 to 4.2 K.

2. Experimental

Polycrystalline samples of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ and $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ were prepared by the solid-state reaction of stoichiometric quantities of Nd_2O_3, $CaCO_3/SrCO_3$, Mn_3O_4 and Fe_2O_3 (99.99% enriched). The mixture was heated at 1173 K, 1273 K

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and 1473 K each for 12 h in air with intermediate grindings. The powder so obtained was pelletized and sintered at 1673 K for 12 h followed by sintering at 1773 K for 12 h in air and oxygen. The phase purity of the samples was ascertained by recording X-ray diffraction patterns with a SEIFERT 3000TT diffractometer. The compounds have the same orthorhombic structures as those of the parent manganates ($Nd_{0.5}Ca_{0.5}MnO_3$, *Pnma*; $Nd_{0.5}Sr_{0.5}MnO_3$, *Imma*). The oxygen stoichiometry of the two compounds was established by redox titrations.

Magnetization measurements were carried out using a vibrating sample magnetometer (Lakeshore VSM 7300) in a field of 100 Oe. Mössbauer spectra were taken in a constant acceleration drive against a 5 mCi ^{57}Co source in Rh matrix, over the temperature range 4.2–300 K using a gas flow helium cryostat. The sample thickness was 19.4 mg of the material/cm^2 (one characteristic thickness of electronic absorption) and the specimen was prepared using thermally conducting GE varnish. To ensure uniformity of absorber thickness, suitable amount of $LiCO_3$ powder was mixed with the material before the specimen was prepared.

3. Results and discussion

On doping $Nd_{0.5}Ca_{0.5}MnO_3$ with 2% ^{57}Fe to give the composition $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ the-charge ordering transition and the Neel temperature were found around 230 and 130 K, respectively (Fig. 1). These transition temperatures are lower than those of the parent manganate, $Nd_{0.5}Ca_{0.5}MnO_3$ [5, 6]. Below 200 K, $Nd_{0.5}Ca_{0.5}Mn_{0.97}{}^{57}Fe_{0.03}O_3$ is reported to exhibit a two-
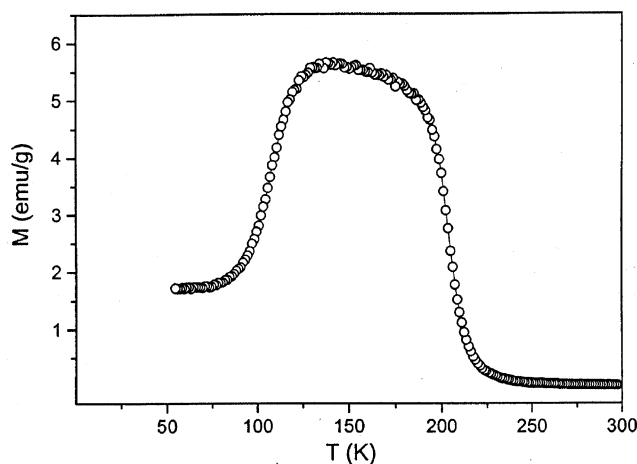
Fig. 2. Temperature variation of the magnetization of $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ showing the ferromagnetic and charge-ordering transitions around 215 and 120 K, respectively.

phase state (with equal proportion of the two), one involving a larger *c* parameter than the other [10]. The long *c* (7.5728 Å) phase remains paramagnetic on cooling to low temperatures while the short *c* (7.5029 Å) phase becomes AFM with a CE-type structure. No drastic changes in lattice parameters are observed across the Neel temperature around 120 K. On doping $Nd_{0.5}Sr_{0.5}MnO_3$ with 2% ^{57}Fe to give the composition $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$, the ferromagnetic transition temperature is lowered ($T_c \sim 215$ K) and the AFM transition occurs around 120 K (Fig. 2). Some samples of $Nd_{0.5}Sr_{0.5}MnO_3$ have been reported to undergo a transition to *A*-type AFM state on cooling the ferromagnetic state below 225 K followed by the transition to the CE-type AFM state below 150 K [8, 9]. At very low temperatures, all the three phases coexist, the highest proportion being that of the CE AFM phase.

3.1. $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$

Mössbauer spectra of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ over the temperature range 295–100 K are shown in Fig. 3. The room-temperature spectrum is a single paramagnetic doublet with an isomer shift (IS) of 0.26 ± 0.01 mm/s and a quadrupole splitting (QS) of 0.20 ± 0.01 mm/s. The isomer shift value is characteristic of Fe^{3+}. On cooling the sample, IS increases gradually and tends to saturate below 130 K as can be seen in Fig. 4(a). The change in the isomer shift with temperature is as expected from the relativistic second-order Doppler shift. It is likely that superimposed on this is the effect of charge ordering giving rise to an effective average valence change and consequent *s*-electron density at the iron nucleus. The spectra retain the doublet character down to 90 K. The line-width increases exhibiting a definitive change below the charge-ordering
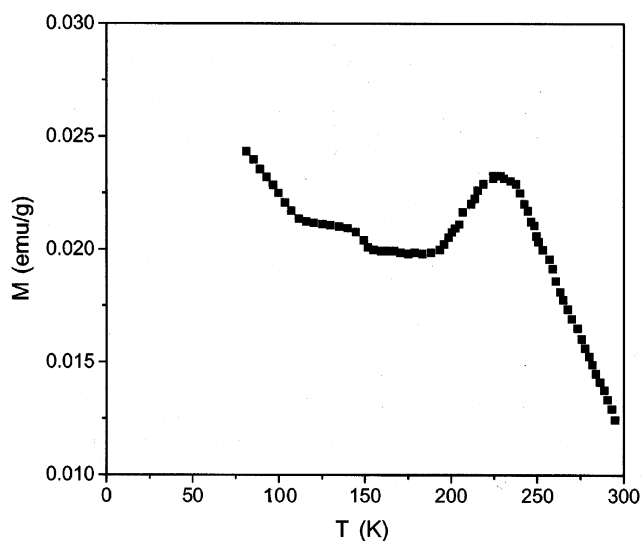

Fig. 1. Temperature variation of the magnetization of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ showing the charge-ordering and AFM transitions around 230 and 130 K, respectively.
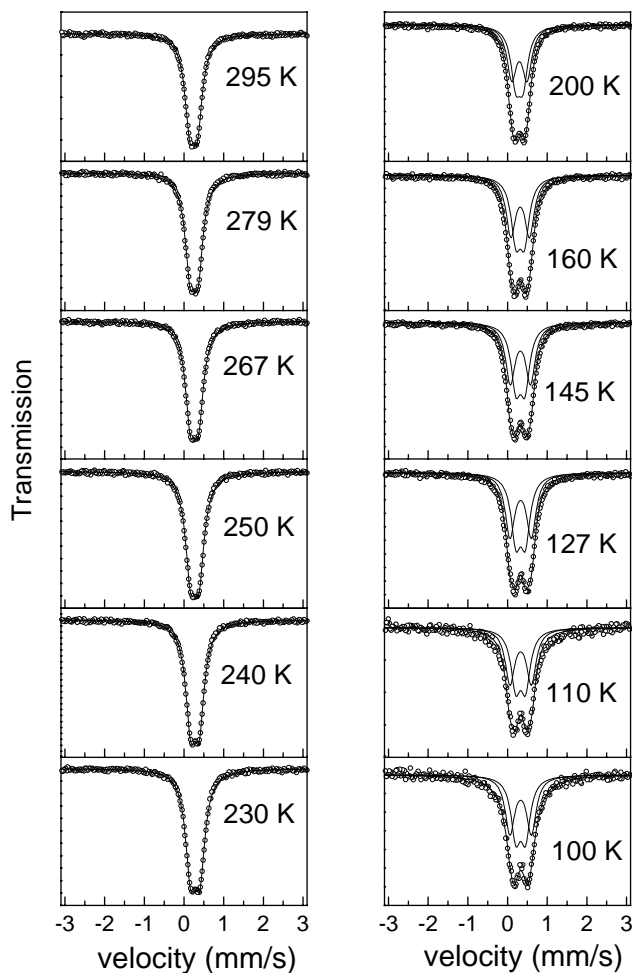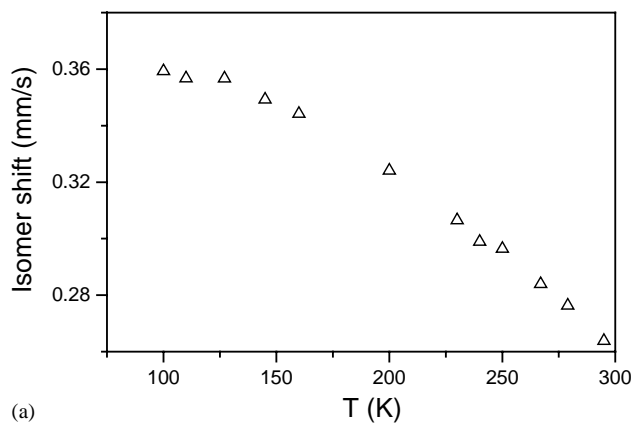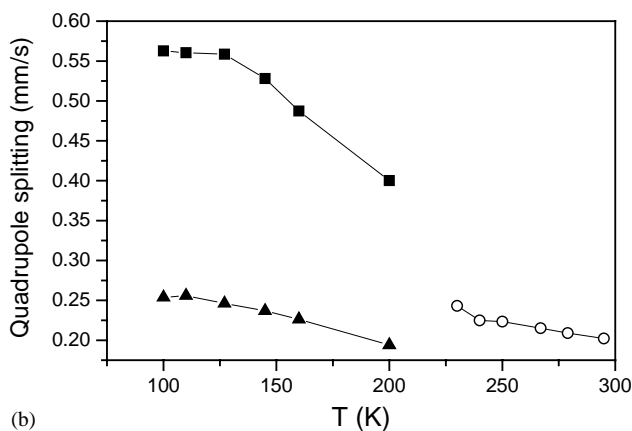
Fig. 3. Mössbauer spectra of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ in the 100–295 K range. Decomposition to two doublets in the 100–200 K range is also shown.

Fig. 4. Temperature variation of (a) the isomer shift and (b) quadrupole splitting of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$. The solid lines are only guides to the eye. In (b), the higher QS is designated as QS1 and the lower one as QS2.

transition at 230 K, as evident from the spectra in Fig. 3. The line broadening below 230 K could either be due to onset of a magnetic order since we observe a peak in magnetization at 230 K, or due to an electronic phase separation suggested in these systems. The onset of short-range magnetic order with relaxation time comparable to the Mossbauer probe time (10^{-9} s) is possible. While the line broadening below 230 K suggests possible magnetic hyperfine interaction, the retention of the doublet-like feature indicates that only short-range magnetic order may exist in the 230–290 K region. The line-width becomes nearly constant around 110 K where the material is known to become a canted antiferromagnet. The Mössbauer spectra in the region 200–100 K are interpreted in terms of two doublets with the same isomer shift, line-width and intensity, but different quadrupole splittings. The fitted subspectra are shown in Fig. 3. A similar behavior has been reported from a study of the Mössbauer spectra of the charge-ordered $Sm_{0.5}Ca_{0.5}Mn_{0.985}{}^{57}Fe_{0.015}O_3$ below the charge-ordering temperature [11].

In Fig. 4(b), we show the temperature variation of the quadrupole splitting in $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$. The quadrupole splitting increases with decrease in temperature showing a jump around 230 K (T_{CO}). This abrupt change in QS below T_{CO} can be related to the charge-ordering transition as is also evident in the magnetization measurements. Abrupt changes in the QS in the Mössbauer spectra around the charge-ordering transition have been reported for $Sm_{0.5}Ca_{0.5}Mn_{0.985}{}^{57}Fe_{0.015}O_3$ [11], $La_{0.5}Ca_{0.5}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ and $La_{0.6}Ca_{0.4}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ [12]. The quadrupole splitting shows two components below 230 K down to 100 K, one with higher QS (QS1) than the room-temperature spectrum and the other with lower QS (QS2). With the lowering of temperature, both QS1 and QS2 increase, but the increase in the value of QS1 is greater than that of QS2. We note that the quadrupole splitting of the lines are temperature dependent, possibly because, the material undergoes structural transition in this temperature region [10]. Both QS1 and QS2 become constant below ~130 K. This is possibly because charge ordering
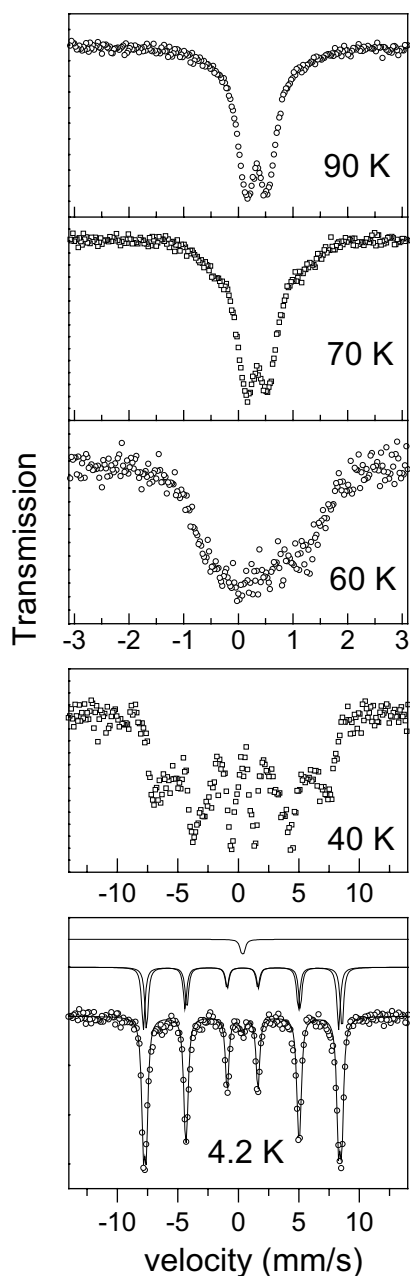
Fig. 5. Mössbauer spectra of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ in the 4.2–90 K range. The spectrum at 4.2 K can be decomposed into three components.

the Fe ions have reached saturating internal fields. We comment upon this spectrum after discussing the results of the Sr-compound below.

3.2. $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$

$Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ shows a single quadrupole doublet at 295 K with an isomer shift of 0.26 ± 0.01 mm/s and quadrupole splitting of 0.30 ± 0.01 mm/s (Fig. 6). The relatively large quadrupolar splitting, QS = 0.30 ± 0.01 mm/s at room temperature has its origin in the orthorhombic distortion [8]. The doublet continues down to 200 K although the isomer shift increases below 250 K as shown in Fig. 7(a). It seems likely that there is some change in the electronic environment around Fe. Accordingly, we note that the line-width is essentially constant down to 220 K and increases below this temperature as shown in Fig. 7(b). The quadrupole splitting also shows a significant increase below ~220 K. The changes found in the line-width below 220 K correspond to the paramagnetic to ferromagnetic

and the structural change are both complete around this temperature. The observation of two quadrupole splittings is consistent with theoccurrence of two phases below T_{CO} [10].

The spectrum at 60 K is broad and unresolved (Fig. 5) possibly indicating a disordered magnetic state, although it could also be due to spin relaxation effects. The spectrum at 40 K shows a six-finger pattern indicative of long-range AFM order, although disorder continues to persist. The spectrum at 4.2 K is, however, well split with reasonably narrow lines indicating that all

Fig. 6. Mössbauer spectra of $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ in the 180–295 K range.
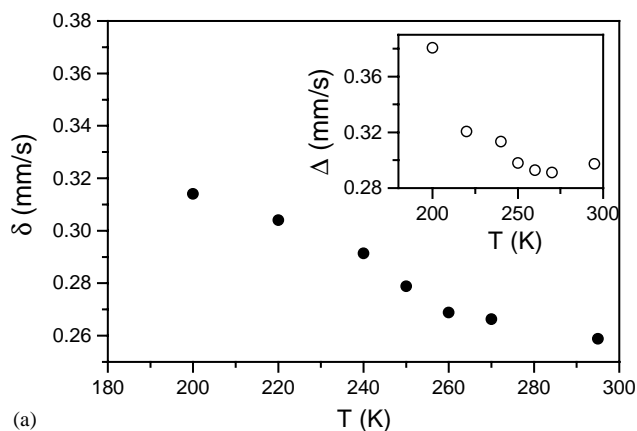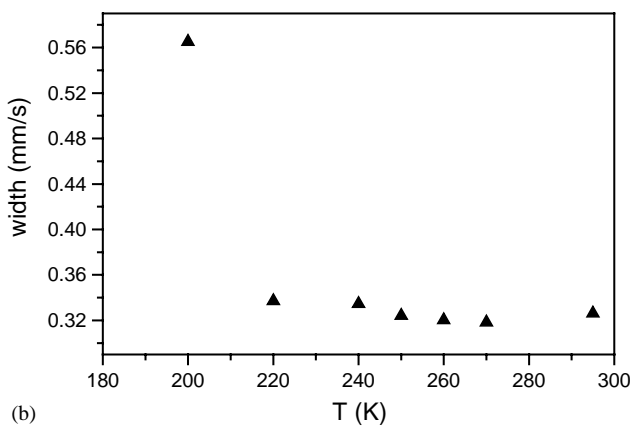
Fig. 7. Temperature variation of (a) the isomer shift and (b) the width of the quadrupole split spectra observed for $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$. The inset in (a) shows the variation of quadrupole splitting as a function of temperature.

transition, although we do not see a clear six-finger spectrum as expected of a long-range ferromagnetically ordered system. There is a definitive and discernible six-finger spectrum below 180 K (Fig. 8), although there is disorder. Compared to $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ the magnitude of disorder may be lower, as evidenced from the resolution of the spectrum at 41 K

The transition to the CE-type AFM state around 120 K (which is evident from the magnetization data) is difficult to discern from Mössbauer spectra (Fig. 8), although the hyperfine features are somewhat more obvious in the spectrum at 100 K. The spectra evolve in a complex manner below 180 K and it is not straight-forward to assign the possible phases present in the 160–40 K range. All the spectra below 160 K show the presence of an unresolved magnetic hyperfine spectrum with an additional central paramagnetic doublet. The evolution of the spectral line shape from 200 K downwards, with an enhanced intensity at the center of the spectrum in the higher temperature range of this region of temperature, is typical of superparamagnetic relaxation. These spectra are similar to those observed by Simopoulos et al. [13] in $La_{0.67}Ca_{0.33}Mn_{0.99}{}^{57}Fe_{0.01}O_3$.
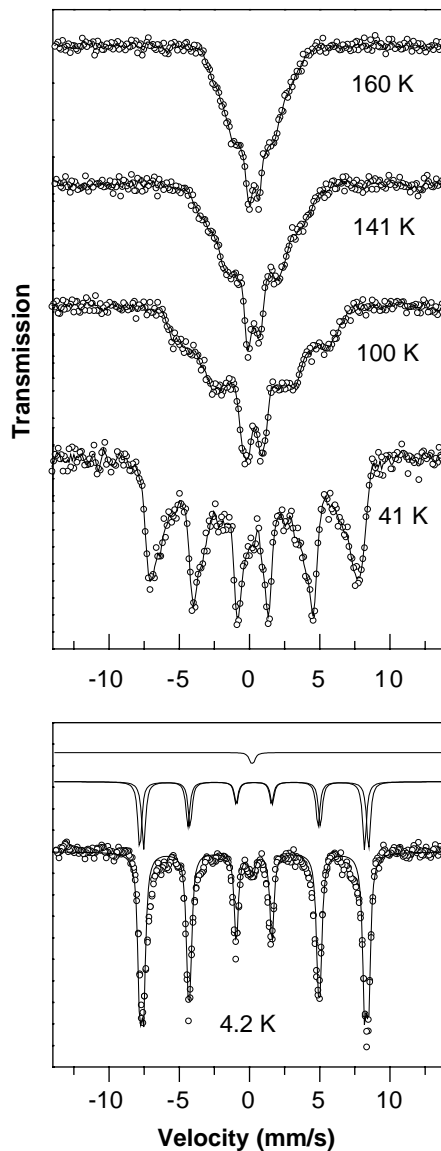

Fig. 8. Mössbauer spectra of $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ in the 4.2–160 K range. The 4.2 K spectrum is fitted with two sextets and a weak paramagnetic doublet

These authors have discussed the various possibilities for the evolution of such line shape in $La_{0.67}Ca_{0.33}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ and have chosen to interpret the observed line shape in terms of the local environmental effects arising from the Fe ions as an "impurity" antiferromagnetically coupled to the ferromagnetic host. With temperature, there is a change in the occupation of localized excited states with reduced total local spin giving rise to the components with reduced hyperfine field. The broadening arises due to thermal population of such states. Applying such a model, they have been able to fit their spectra with a set of discrete distribution of hyperfine fields at various temperatures. However, we consider superparamagnetic relaxation being the cause of the observed line shape evolution of $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$. Simopoulos et al. [13]

remark that the Mössbauer spectra can be reproduced using the well-known spin relaxation model of van der Woude and Dekker [14]. The only objection to this model is that it is not consistent with the 3D Heisenberg ferromagnetic behavior in their sample indicated by neutron experiments [13]. This is not a serious objection, as the Fe probe may not behave in a manner identical to that of Mn with respect to electronic relaxation and may not participate in the double-exchange mechanism of Mn ions. Thus, it is possible that the Fe ion may not follow the bulk magnetic property of the system, but instead reflect its own dynamics with respect to its neighboring ions. We, however, see a well-resolved magnetic hyperfine spectrum at 4.2 K (Fig. 8). Thus, Mössbauer spectra show that long-range magnetic order does not emerge in a clean manner in this manganate as well.

We now discuss the spectra at 4.2 K of the two manganates. We see a well-resolved magnetic hyperfine spectrum with reasonably narrow line-width in both the cases. This observation implies either that the long-range order sets in or that the superparamagnetic relaxation reaches its end. It is to be noted that the Mössbauer spectrum for an antiferromagnetic or a ferromagnetic system would be very similar as the Fe nucleus essentially senses the local spin. Considering that there could be a small difference in the field at the nucleus due to local spin environment, and assuming that the saturation field has been achieved at 4.2 K, we have deconvoluted the slightly broadened spectra in terms of two equal intensity hyperfine spectra. The spectra at 4.2 K do not show appreciable asymmetry and hence no appreciable quadrupolar interaction in the low-temperature phases. The hyperfine field, H_{int} of the two magnetic phases for $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ are 488 and 506 kOe and their respective isomer shifts are 0.38 and 0.39 mm/s. In the case of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$, the hyperfine field, H_{int}, of the two magnetic phases are 487 and 503 kOe and their respective isomer shifts are 0.39 and 0.40 mm/s. The spectra are consistent with the presence of two phases arising from electronic phase separation. Both the spectra also show a weak central paramagnetic component. This may be one of the phase-separated components or in an unlikely event, a small impurity phase.

4. Conclusions

The present study of the temperature evolution of Mössbauer spectra of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$

and $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ shows that long-range magnetic order does not emerge in a conventional manner in both the manganates. In the case of $Nd_{0.5}Ca_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$, the spectra in the high-temperature region could be interpreted in terms of two doublets arising due to the presence of two phases below the charge-ordering temperature. Below the magnetic-ordering temperature, the evolution of magnetic order in this manganate resembles that of a disordered system. In the case of $Nd_{0.5}Sr_{0.5}Mn_{0.98}{}^{57}Fe_{0.02}O_3$, the spectra below T_N are not unlike that of a superparamagnetically relaxed system, even though clear bulk magnetic order is observed in this system. Well-resolved magnetic hyperfine Mössbauer spectra occur at 4.2 K in both the manganates, with a slight broadening of the lines. The spectra can be deconvoluted into two spectra, which are consistent with the occurrence of electronic phase separation.

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