

Phase separation in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$: a Mössbauer study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 1665

(<http://iopscience.iop.org/0953-8984/16/9/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 07:54

Please note that [terms and conditions apply](#).

Phase separation in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$: a Mössbauer study

S C Bhargava¹, Sher Singh¹, D C Kundaliya² and S K Malik²

¹ Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

² Tata Institute of Fundamental Research, Colaba, Mumbai 400 005, India

Received 30 July 2003

Published 20 February 2004

Online at stacks.iop.org/JPhysCM/16/1665 (DOI: 10.1088/0953-8984/16/9/014)

Abstract

Mössbauer spectroscopy of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ shows phase separation above and below the magnetic transition temperature T_C . These phase separations are found to be independent and related to different phenomena. The relative volumes of the two phases above and below T_C are also very different. Mössbauer spectra above T_C show that the phase splitting is due to different lattice distortions around Fe in the two phases. The paramagnetic component showing large distortion disappears when the magnetic hyperfine splitting appears on lowering the temperature. The phase splitting below T_C is due to a difference in the nature of magnetic ordering and the degree of covalence of the magnetic ions in the two phases. DC magnetization shows that the spin ordering in the two phases is collinear and non-collinear, respectively. At low temperatures, the non-collinear phase converts into the collinear phase when the applied magnetic field exceeds a certain value. When the field is withdrawn, the non-collinear phase is not fully regained.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Manganite $\text{R}_{1-x}\text{D}_x\text{MnO}_3$, with R a trivalent rare earth or Bi^{3+} cation and D a divalent alkaline or Pb^{2+} cation and possessing perovskite structure, shows interesting behaviour as x is varied. The perovskite $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $0.25 < x < 0.5$, shows a metal–insulator (MI) transition at low temperature (T_P), associated with a large colossal magnetoresistance (CMR) [1–7]. This has important applications in the magnetic recording industry [8]. In the other regions of x , phenomena like charge and/or orbital ordering occur which are interesting from a basic research point of view [9–13]. Initially, the double exchange theory was thought to adequately describe the MI transition [14–16]. Subsequently, the roles of Jahn–Teller distortion [17], polaron formation [18], etc, were investigated. The importance of phase separation to CMR has been emphasized in recent studies [1]. In the present study, these phases are studied using the microscopic method of Mössbauer spectroscopy.

The effects of substitution of the Mn ions with d^n and non- d^n elements on the ferromagnetic coupling between $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ due to the e_g band have been extensively studied [19]. The dopant with d^n outer shell ($n \neq 0, 5, 10$) affects the e_g band and increases the metallic character. On the other hand, the valence electrons of the other elements do not take part in the e_g band and, therefore, inhibit the passage of the e_g electrons through the impurity sites. This increases the antiferromagnetic coupling around the impurity site. The increase in frustration with the substitution eventually leads to a spin glass (SG) ordering of spins. The substitution of the R ions with other trivalent cations (magnetic or non-magnetic) has also been found to greatly affect the behaviour of the parent oxide, even though the magnetic properties are dependent on the Mn–Mn interactions [20–25]. This is because the different size of the impurity ions induces strain in the lattice, which results in a deviation of the $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ angle from 180° . This reduces the strength of the ferromagnetic coupling, decreases T_C and eventually leads to SG ordering [20–25].

Associated with the decrease in T_C is an increase in CMR. Recent studies have shown this to be a direct consequence of an electronic phase separation [1, 26–29] into a non-collinear charge ordered (CO) phase and a ferromagnetic (FM) phase. It has been found that typical sizes of the CO and FM phases at low temperatures are of the order of several thousand ångströms. At higher temperatures, $150 < T < 220$ K, a nanoscale mixture of CO and FM phases coexists. It is further shown by the electron diffraction method that the superlattice peaks of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $x = 1/2$, occur even in the composition with $x \approx 0.375$. The difference in the carrier concentration is accommodated by charge defects in the $x = 1/2$ -type CO state. Thus, the phase separation relevant to CMR is between FM and the $x = 1/2$ -type CO state. The balance between these two states, with different electronic properties, can be readily influenced by varying physical parameters such as an applied magnetic field, hydrostatic pressure [30–32], chemical pressure, or oxygen isotope. The two-phase situation can also be influenced by the cooling rates across the ordering temperature. Measurement of M after quick cooling shows time dependence, obeying stretched exponential form, indicating a distribution of relaxation times. The relevant timescale is of the order of a few hours. The temperature dependence of the relaxation shows that it is a thermal activation type. The thermal activation barrier is large if the field required to melt the CO state is large, as is the case near $x = 1/2$. Large structural anisotropy results due to the cooperative Jahn–Teller distortion in the CO phase. Thus, there is a deformation of the parent crystal surrounding the CO phase, which is called accommodation strain. Consequently, the CO phase cannot grow at the domain boundary. Thus, when the domain size is reduced, the fraction of FM phase relative to the CO phase decreases. As a result, the properties have been found to depend strongly on the grain size too. In small particle of $3 \mu\text{m}$ size, the FM phase does not appear even at 20 K.

In the present study, we investigate the phase separation in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ using Mössbauer spectroscopy. The microscopic nature of this method can reveal properties of the electronic phases that can help our understanding of this interesting phenomenon. In the parent oxide $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, MI transition occurs [33] at $T_P \approx 245$ K, and CMR in a field of 6 T has been found to be 115%. The substitution of Mn with Fe produces drastic changes even though Mn^{2+} and Fe^{3+} have almost identical sizes. The increase in Fe increases the resistivity, and decreases T_P . Cai *et al* [33] found that a 10% substitution leads to a change in the resistivity by six orders of magnitude, T_P decreases to 45 K, and CMR in a field of 6 T was found to be $3.5 \times 10^5\%$. The AC susceptibility showed a peak at 42 K, which moved to lower temperatures and decreased in height as the DC field was increased. The peak showed dependence on the frequency of the AC field also. The magnetic measurements of Cai *et al* [33] thus indicated a spin glass ordering in the metallic state at $T < 45$ K.

A neutron diffraction study of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ [34], however, gave different results. A comparison of the powder neutron diffraction patterns at 125 K, where the substance is paramagnetic, and 15 K, where the oxide is magnetic, showed negligible magnetic contribution to the Bragg peaks at 15 K. Thus, the absence of a long-range magnetic ordering at 15 K was found. However, the neutron depolarization measurements showed a decrease in the neutron polarization on lowering the temperatures below 108 K. The field cooled (FC) and zero-field cooled (ZFC) magnetizations, determined using a DC field of 100 Oe, showed branching at ≈ 80 K [34], which is higher than the branching temperature of 43 K found by Cai *et al* [33]. In the investigations of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ by Kundaliya *et al* [35] also, disagreement with the results of Cai *et al* [33] was found. In view of the high sensitivity of the properties of the oxide on the preparation procedure and x in this range of concentration, even slight differences can be responsible for the disagreement found. Hasanain *et al* [36] made magnetic and transport measurements on $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$. The resistivity changes are found to be gradual and linear below 4% doping, while above this concentration the changes are found to be large. At 4% doping, the Fe–Fe separation begins to be comparable to the size of the charge carriers [36]. Between 8 and 10% substitution, the resistivity changes by two orders of magnitude and T_P decreases by 30 K. The T_P of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ was found to be higher than 77 K, in disagreement with the results of Cai *et al* [33]. We have not mentioned the studies in which the Fe concentration was less than 5%. This is because in these cases the resistivity in the metallic state is low. This has two consequences. First, CMR is not high in these substances. Second, spin relaxation effects are not observable in the Mössbauer spectra. Unlike such oxides, we are investigating a composition, which shows large CMR and in which spin relaxation affects the Mössbauer spectra.

It is thus seen that the studies done so far on $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ have provided contradictory results. The phenomenon of the phase separation that is crucial [1] to our understanding of CMR was not addressed in any of the earlier investigations of the Fe-doped manganite. In the present study of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$, we have been mainly concerned with this aspect. We have made AC and DC susceptibility measurements to characterize the sample well. We use the microscopic method of Mössbauer spectroscopy to characterize the two phases, which appear above and below T_C , taking into consideration the presence of relaxation effects. The properties of the two phases are thus determined.

2. Experimental details

We followed the solid-state reaction method used in [37]. La_2O_3 was heated to 1000 °C. Subsequently, La_2O_3 , CaCO_3 , $^{57}\text{Fe}_2\text{O}_3$ and MnO_2 were mixed in the desired proportions and heated at 1100 °C, with intermediate grindings, for 48 h. Subsequently, it was heated at 1300 °C for 48 h, with an intermediate grinding.

The resistance was measured using the standard four-probe method in the presence of fields up to 6 T. Magnetization measurements were made using a commercial SQUID magnetometer (Quantum Design). FC and ZFC magnetizations were obtained using DC fields of 50 and 5000 Oe. AC susceptibility measurements were made using frequencies in the range from 10 to 1500 Hz and superimposed DC fields of 0 and 40 Oe, using a SQUID magnetometer.

Mössbauer spectra have been obtained using a cryogenic set-up described elsewhere [38, 39]. A ^{57}Co source in Rh matrix of 50 mCi strength has been used in the measurements. The temperature is controlled to $\pm 0.1^\circ$ with a carbon glass resistor and measured using a platinum resistance thermometer. The calibration spectrum of Fe foil showed lines of ≈ 0.3 mm s^{-1} full width.

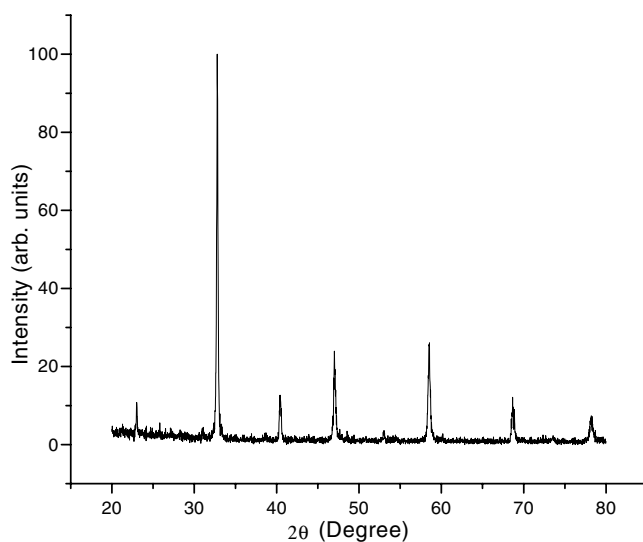


Figure 1. X-ray diffraction pattern of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

3. Results

The analysis of the x-ray diffraction pattern (figure 1) showed the formation of a single-phase perovskite structure with $a = 3.856 \text{ \AA}$, $b = 3.863 \text{ \AA}$, and $c = 3.876 \text{ \AA}$, in good agreement with the results of Cai *et al* [33]. The temperature dependence of the resistance was measured, using the standard four-probe method, in the presence of magnetic fields up to 6 T (figure 2). The temperature dependence observed is similar to behaviour observed by Cai *et al* [33]. The metal–insulator transition is very well defined. At low temperatures, the oxide becomes an insulator again. In the presence of a field of 6 T, T_p is 75 K and the oxide becomes an insulator again at temperatures lower than 30 K. The metallic behaviour is seen in the temperature range from 30 to 75 K. The shape of the R versus T curve is not expected to change at lower magnetic fields, though T_p decreases and the MI transition becomes narrower. The decrease is large if CMR is large. In the present case, however, the observed sharp increase in resistance in zero field shows that T_p is not appreciably different in lower magnetic fields.

AC susceptibilities measured, using an AC field of 0.5 Oe and frequency 100 Hz, in the presence of DC fields of 0 and 40 Oe, are shown in figure 3. The peak temperature is 85 K. In addition there is a peak at 65 K. The two peaks appear to be due to the presence of two phases coexisting in this temperature range. The effect of the DC field is insignificant in comparison to the effect found by Cai *et al* [33] and in other spin glasses. Similarly, the AC susceptibility in a DC field of 1 Oe is not significantly affected (figure 4) by a change in the frequency of the AC field, in the range from 10 to 1000 Hz. This is different from the behaviour shown by spin glasses and the results of Cai *et al* [33]. Our results are in agreement with the observations of Kundaliya *et al* [35]. The peak in the AC susceptibility is broad in the results obtained by Kundaliya *et al* [35], probably due to the low sintering temperature of 1100 °C used by them. As a result, the two peaks were not distinctly visible in their experiment. It is thus found that $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ is not a spin glass. FC and ZFC magnetizations obtained using DC fields of 50 and 5000 Oe are shown in figures 5(a) and (b). The branching temperatures are found to be 80 and 50 K, respectively. It may be remarked here that $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$,

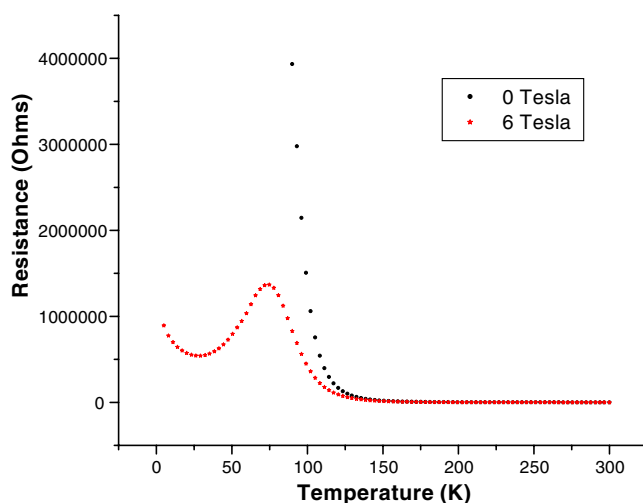


Figure 2. The temperature dependence of resistance of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ in the presence of magnetic fields of 0 and 6 T.

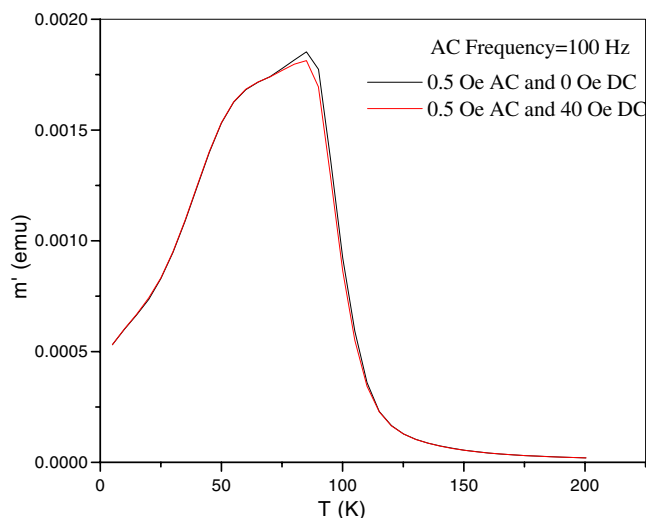


Figure 3. AC susceptibilities measured using an AC field of 0.5 Oe and frequency 100 Hz, in the presence of DC fields of 0 and 40 Oe.

which shows ferromagnetic ordering at 245 K, also shows the branching of FC and ZFC magnetizations at the ferromagnetic ordering temperature [33].

DC magnetization showed linear dependence on the magnetic field and is reversible at 300 K (figure 6). At 150 K, slight nonlinearity appears. At 75 K, the magnetization increases sharply as the field appears and slowly beyond 2 kOe, showing that 75 K is below the magnetic ordering temperature. The magnetization is fully reversible at 75 K also. At 5 K, remarkably, the magnetization is not reversible. Thus, the effect of increasing the magnetic field at 5 K is not merely a change in the non-collinearity angle, but also a conversion of the non-collinear phase into FM phase. The conversion is not reversible. This shows the metastable nature of

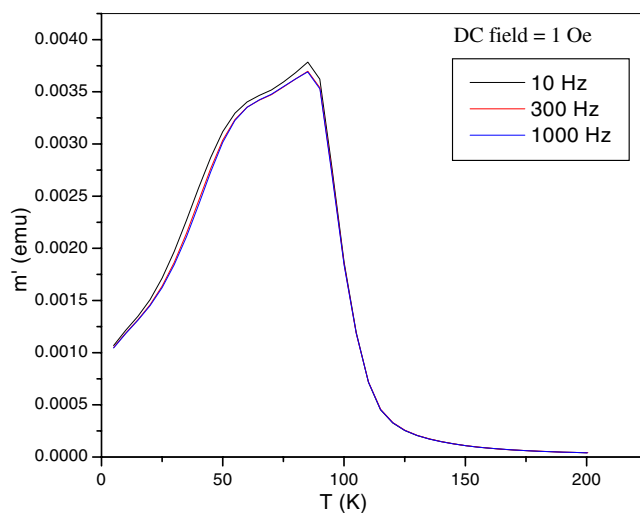


Figure 4. AC susceptibilities in a DC field of 1 Oe and AC field of 0.5 Oe at different frequencies.

Table 1. Results of analysis of Mössbauer spectra of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ in the paramagnetic state.

Temperature (K)	Component 1			Component 2		
	QS (mm s^{-1})	CS (mm s^{-1})	RI (%)	QS (mm s^{-1})	CS (mm s^{-1})	RI (%)
298	1.32	0.38	3.4	0.24	0.35	96.6
110	—	—	—	0.33	0.33	100

the FM phase at low temperatures. At present, the reason for this phenomenon is not well understood.

The Mössbauer spectrum in the paramagnetic state is remarkable. The spectrum at ambient temperature shows two doublets, even though Fe ions occur at equivalent sites (table 1). The possibility of an impurity phase was ruled out from the following considerations. First, the doublet with larger QS is found in the paramagnetic Mössbauer spectrum of $(\text{La}_{1-x}\text{Dy}_x)_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.97}\text{Fe}_{0.03}\text{O}_3$ also, prepared using either the solid state reaction or wet method. Second, the temperature dependence showed that the weaker doublet disappears at T_C (figure 7). This characteristic of the weaker doublet was shown by the paramagnetic spectra of $(\text{La}_{1-x}\text{Dy}_x)_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.97}\text{Fe}_{0.03}\text{O}_3$ also. This conclusively showed that the weaker doublet is not due to an impurity phase. The paramagnetic spectrum is fitted with two symmetric doublets, without taking into consideration the thickness correction. This leads to an underestimation of the relative intensity (RI) of the stronger doublet. Even if the correct value of the RI of the stronger doublet is higher by 25%, the RI of the two doublets will change from 4:96 to 3.44:96.56. This will not alter the conclusions obtained in the present study that the phase splitting occurs in the paramagnetic state also and the weaker doublet disappears when the temperature is lowered to T_C .

Mössbauer spectra at temperatures lower than 100 K show magnetic hyperfine splitting (figure 8). The lines are broad and the spectral shape anomalous. Our earlier studies on mixed oxides, with high resistivities and random distribution of cations, have shown the presence of single-ion spin relaxation. The relaxation times are found to be weakly dependent on

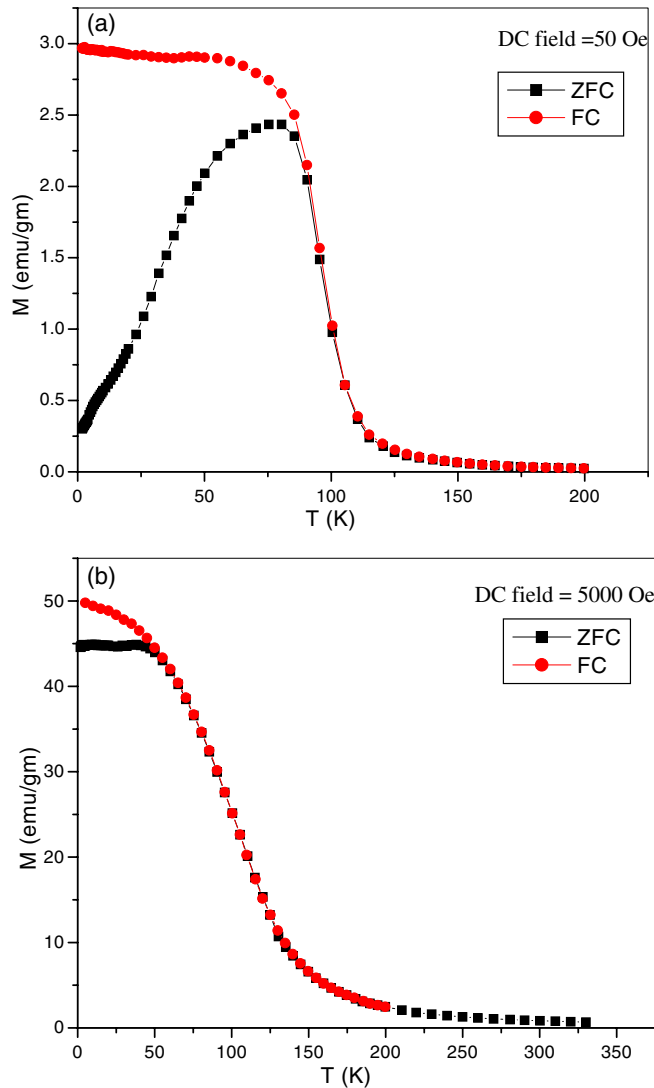


Figure 5. (a) and (b): FC and ZFC magnetizations obtained using DC fields of 50 and 5000 Oe, respectively.

temperature and of the order of a nanosecond. On the other hand, in non-oxide substances with low resistivity, the relaxation times are very small ($\approx 10^{-12}$ s). In such a case, the effects of relaxation on a Mössbauer spectrum are negligible. The line shape is a sextet due to static hyperfine fields. The anomalous shape observed in the spectrum of such a substance is due to variation in the hyperfine fields. An important difference in the effects of the two causes of the anomalous Mössbauer line shape is the following. In the presence of single-ion spin relaxation, the ratios $(\delta_{34}/\delta_{16})$ and $(\delta_{25}/\delta_{16})$ decrease as T_C is approached [40]. Here, δ_{ij} represents the separation between i th and j th lines of a Mössbauer spectrum. In contrast, in the anomalous shape due to a distribution of hyperfine fields, this ratio is independent of temperature. This difference enables us to uniquely determine the cause of the anomalous shape of a Mössbauer

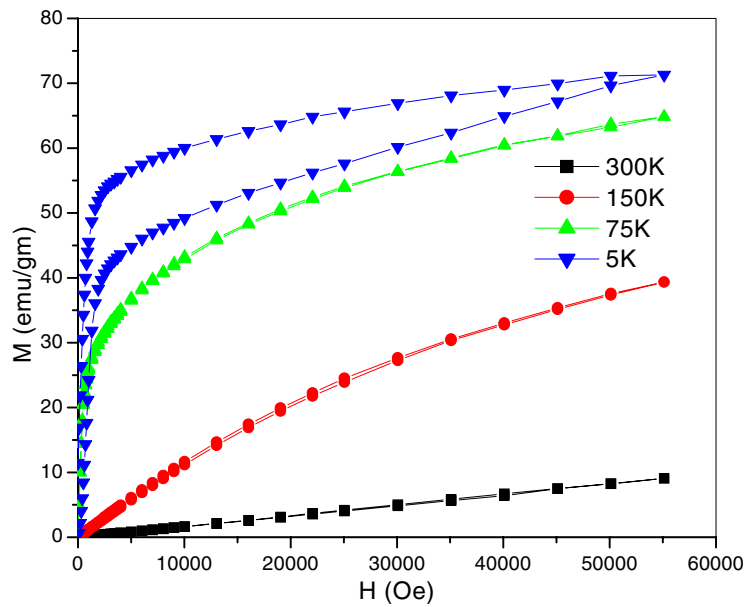


Figure 6. DC magnetizations at different temperatures change as the field is increased and then decreased, as shown in this figure. The irreversibility at 5 K is remarkable.

spectrum. In the present study, as well as in the earlier studies of the disordered oxides, it has been found that the cause of the line broadening and anomalous shapes of the Mössbauer spectra is single-ion spin relaxation (hereafter referred to as spin relaxation).

Even though the oxide under study shows a metallic behaviour in the temperature range from 30 to 70 K, the resistivity is very high even in this range of temperature [33]. Spin relaxation times are, therefore, expected to be large, and affect the Mössbauer spectrum. Evidence for this is provided by anomalous Mössbauer spectra which show a temperature-dependent ratio (δ_{34}/δ_{16}), which decreases at temperatures greater than 30 K. We have fitted the experimental spectra using the stochastic model of single-ion spin relaxation, described elsewhere [38–45]. The spectrum depends on the relaxation time (RT), $\langle S_Z \rangle$, $H_{\text{int}}(T = 0)$, quadrupole shift [$\epsilon(M) = (\delta_{12} - \delta_{56})/(4)$], relative line intensities and the line widths (Γ). The ratio of the thermal populations of the successive ionic Zeeman levels, known as the s -parameter, provides $\langle S_Z \rangle$.

The lowest temperature at which a Mössbauer spectrum is obtained in the present study is 6.5 K. At this temperature ($T/T_C < 0.1$), the relaxation broadening is small. The relaxation time cannot be determined from such a spectrum. This is because at such low temperatures, only the lowest ionic Zeeman level is populated. As a result, the relaxation cannot affect the Mössbauer spectrum. Such spectra yield accurate values of the relative line intensities and natural line widths when there is only one component sextet. When the spectrum consists of two strongly overlapping sextets of comparable intensities, as in the present study, it is not possible to determine relative intensities and widths in the component sextets using the least squares procedure. In view of this, line widths and relative line intensities are constrained to reasonable values. Furthermore, the two sextets are assumed to have equal relative line intensities and line widths. The depth of the outer lines at low temperature is small and comparable in the two sextets. It is, therefore, not necessary to include a thickness correction to analyse the magnetic spectra. With all these assumptions, this spectrum is used to obtain

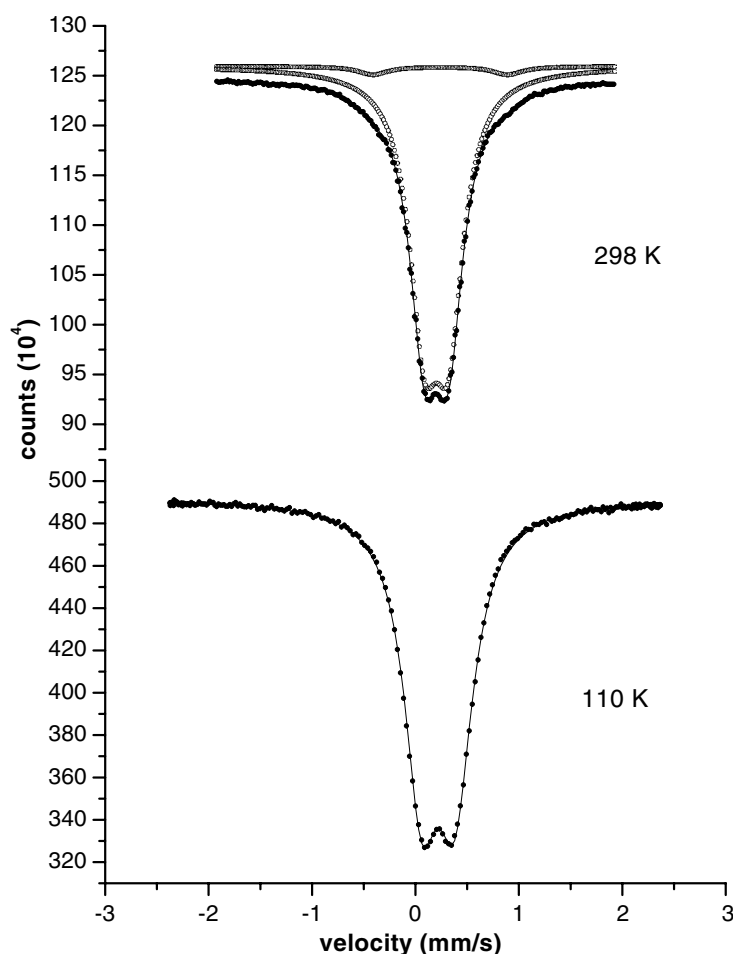


Figure 7. Mössbauer spectra of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ in the paramagnetic state at ambient temperature and 110 K.

$H_{\text{int}}(T = 0)$, $\epsilon(M)$, centre shifts, line widths (Γ), and the relative intensity of the two sextets. With these sets of parameters, we attempt to fit the higher-temperature spectra, by treating only the s -parameters and relaxation times as the variable parameters. If the choice of parameters to fit the low-temperature spectra is not good, it becomes impossible to fit higher-temperature spectra. In such a case, the low temperature spectrum is refitted by suitably changing the line widths and relative line intensities. This procedure is repeated until spectra at all temperatures can be fitted by treating only the s -parameters and relaxation time as the variable parameters. It is, however, found to be impossible to fit the spectra in the temperature range from 30 to 70 K by treating the line widths as temperature independent: the reason for this appears to be the change in the transport properties of the oxide in the temperature range from 30 to 80 K, where the oxide shows metallic character. The greater metallic character implies larger variation in hyperfine fields due to the variation in the environment of Fe. This appears as line broadening. However, unlike other metallic substances, the resistivity of the manganite is high ($\approx 10^5 \Omega \text{ cm}$) even in this range of temperature. As a result, it has been possible to get excellent fits to the spectra in the temperature range 30–70 K also, though using larger

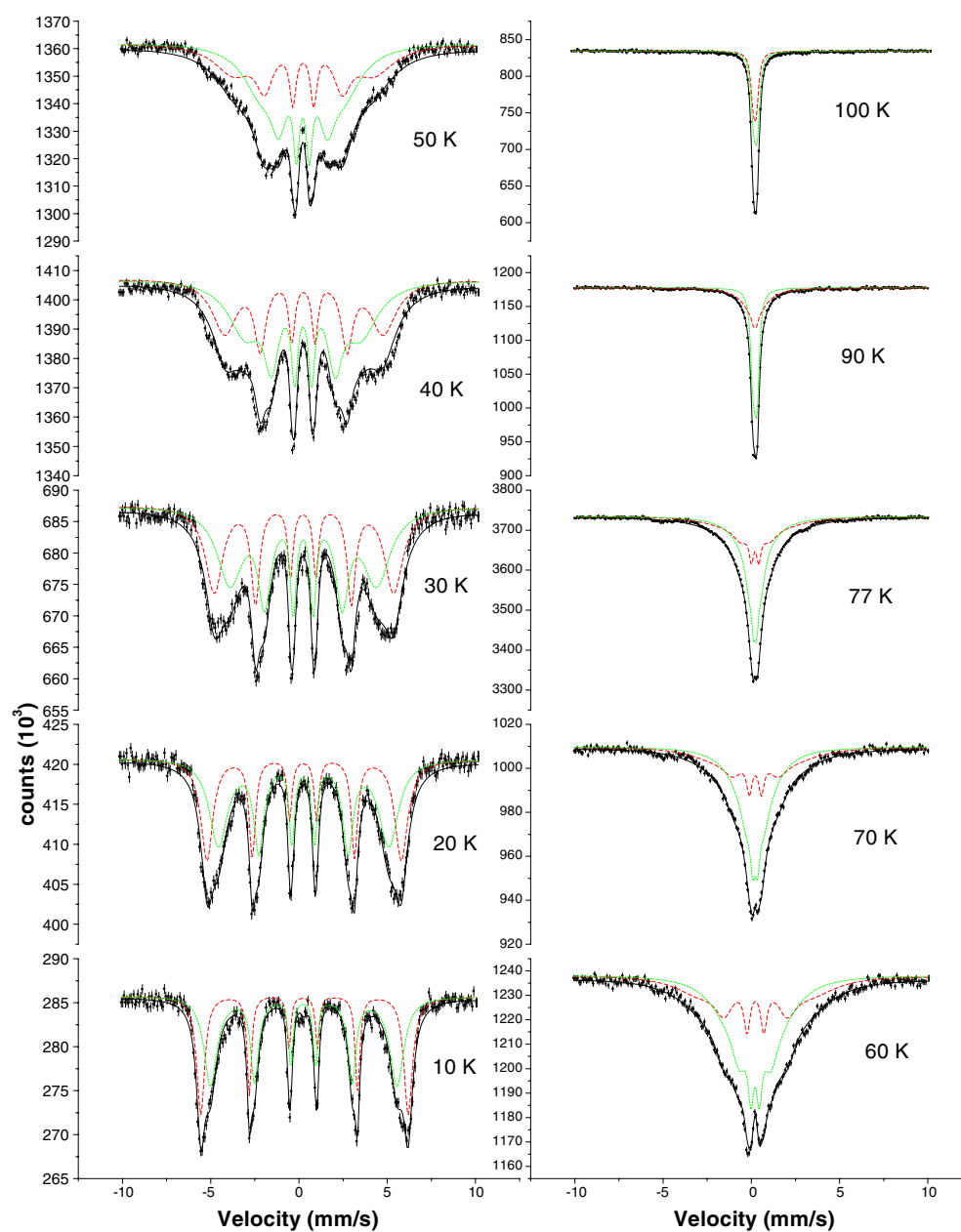


Figure 8. Mössbauer spectra of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ at temperatures below 100 K. The theoretical spectra that fit best are shown with black solid curves. Component A are shown by dashed curves and the component B are shown by dotted curves.

line widths. The fits thus obtained are shown in figure 8. The temperature dependences of $\langle S_z \rangle$ and the relaxation times of the Fe ions in the two phases are shown in figures 9 and 10, respectively. The transition temperature is thus found to be close to 108 K, as found from the neutron depolarization studies [34]. The temperature dependences of the widths of the outer

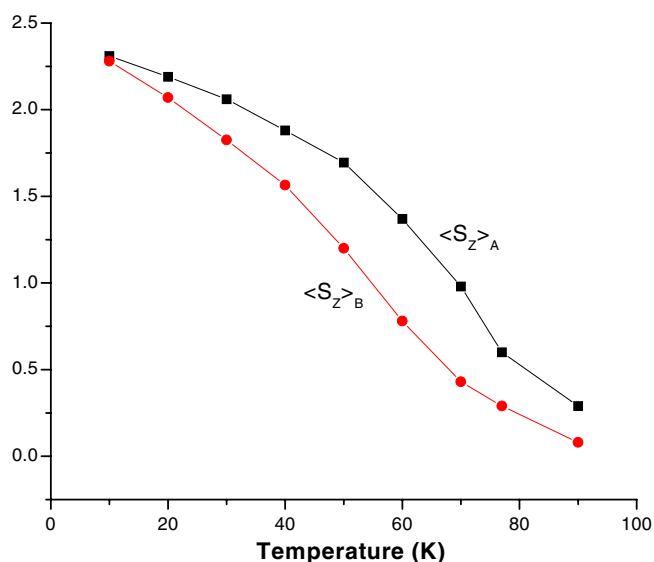


Figure 9. The temperature dependences of $\langle S_Z \rangle$ of the Fe ions in the two phases of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

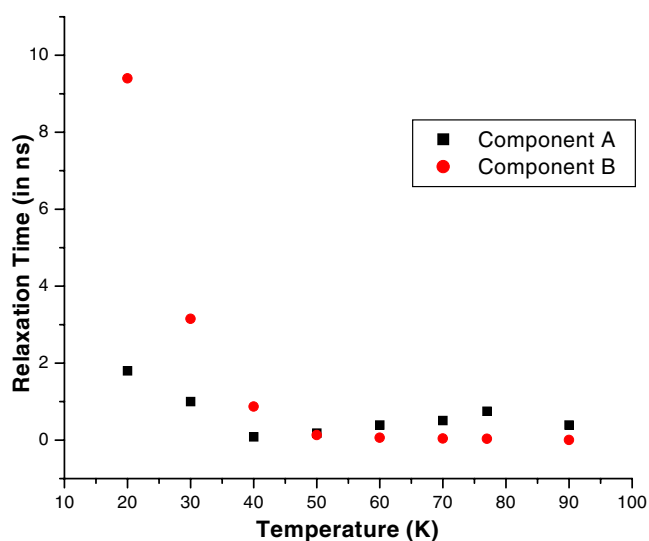


Figure 10. The temperature dependences of the relaxation times of Fe ions in the two phases of $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

lines of the two sextets, assumed equal, are shown in figure 11. The parameters characterizing the A-component are thus found to be: $H_{\text{int}}(A, T = 0) = 535$ kOe, $\epsilon(M) = -0.011$ mm s $^{-1}$, $I_{16}:I_{25}:I_{34} = 3.0:2.0:1.0$, and the relative intensity = 40%. The parameters characterizing the B-component are found to be: $H_{\text{int}}(B, T = 0) = 469$ kOe, $\epsilon(M) = -0.02$ mm s $^{-1}$, $I_{16}:I_{25}:I_{34} = 3.0:2.0:1.0$, and the relative Intensity = 60%. The relative intensity of the two phases, assuming the f -factor to be same in the two phases, is thus found to be 4:6.

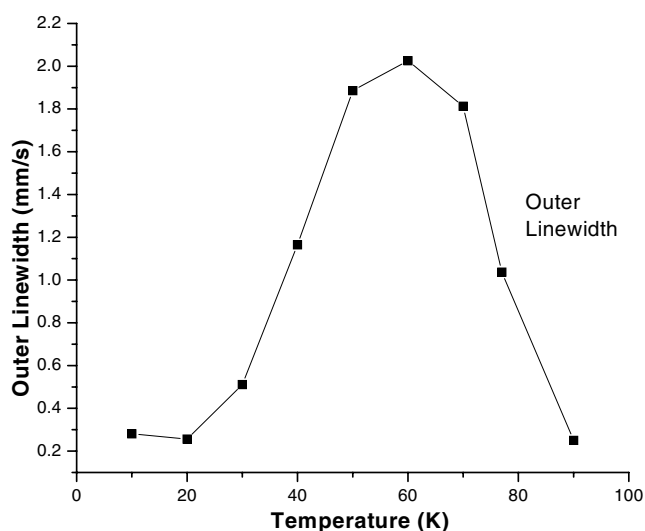


Figure 11. The temperature dependences of the widths of the outer lines in the two-component Mössbauer sextets of Fe in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$.

Here, $\epsilon(M) = (\delta_{12} - \delta_{56})/4$. The centre shifts of the two sextets differ by 0.016 mm s^{-1} and show Fe to be in the high-spin Fe^{3+} state in both the phases.

4. Discussion

In the undoped oxide, we have a lattice of Mn^{3+} and Mn^{4+} ions coupled ferromagnetically due to the hopping of the e_g electrons. When Fe substitutes Mn partially, it creates a nonconducting path to the electron hopping and tends to be antiferromagnetic to the neighbouring ions. As a result, the resistivity increases and T_P decreases. Thus, T_C also decreases. In the picture that has emerged from recent studies, there is a coexistence of a non-collinear CO and FM phases. The substitution changes the relative volumes of the two phases and decreases the magnetic ordering temperature T_C rapidly.

In $\text{La}_{0.66}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$, we see phase splittings at temperatures above and below T_C . The two splittings are, however, independent. The relative volumes of the two phases above and below T_C are also very different. Above T_C , the splitting into two phases is found in the Mössbauer study of $(\text{La}_{1-x}\text{Dy}_x)_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.97}\text{Fe}_{0.03}\text{O}_3$ also. Remarkably, the weaker spectrum with large QS disappears when the temperature is lowered to T_C . The QS of the weaker doublet shows the presence of a large distortion in the neighbourhood of Fe. It thus appears that this part of the manganite shows Jahn–Teller distortion, which disappears at the magnetic transition temperature. The other doublet, which has larger relative intensity, has low QS and thus shows the absence of a significant distortion around Fe in this phase. Our results thus show that only a small part of the lattice shows Jahn–Teller distortion above the magnetic ordering temperature. The other part has negligible distortion.

Our results provide direct evidence of the formation of two phases below the magnetic transition temperature T_C . The characteristics of the two phases have been studied using macroscopic methods in earlier studies. In the present investigation, we use the microscopic method of Mössbauer spectroscopy and determine the characteristics of the two phases. The Mössbauer spectral shapes are, however, complex. We have succeeded in fitting the

complicated shapes accurately over the entire range of temperature, using the stochastic model of single-ion spin relaxation. The fits obtained in the insulating phase are good and show behaviour similar to that found in other insulators. In the metallic phase also, the fits to the experimental spectra are good. The experimental line widths increase with metallicity (figure 11). The experimental line width $\Gamma(T)$ can be expressed as a sum of three contribution:

$$\Gamma(T) = \Gamma(T = 0) + \Gamma_{\text{non-relaxation}}(T) + \Gamma_{\text{relaxation}}(T).$$

The contribution to the width due to single-ion spin–spin relaxation is temperature independent, as is found in other disordered oxides. Thus, the observed temperature dependence appears to be due to $\Gamma_{\text{non-relaxation}}$ only. The maximum occurs in the temperature range from 50 to 70 K. Resistance too shows metallic behaviour in this temperature range (figure 2). Earlier studies have shown that the hyperfine magnetic field variation as a result of a variation in the neighbourhood is negligible in insulators, but is large in metallic substances. Thus, when a substance becomes metallic, the variation in hyperfine field increases. This variation in hyperfine fields appears as line broadening and is represented by $\Gamma_{\text{non-relaxation}}$.

The centre shifts of the two sextets differ insignificantly, showing that the two sextets correspond to the same charge state of Fe. Quadrupole shifts in the two sextets are small and not significantly different, possibly due to little structural distortion around Fe below T_C . The internal magnetic fields in the two phases are significantly different: 535 and 470 kOe.

An obvious distinction between the two phases is the collinear and non-collinear magnetic ordering in them. In view of the randomness in the distribution of the magnetic ions in the two phases, the non-collinear ordering is unlikely to be antiferromagnetic. Further, AC susceptibility does not show a dependence on the frequency of the AC field or the value of the DC field. Thus, we can rule out spin glass ordering to be the nature of the non-collinear ordering. At low temperatures, the non-collinear phase converts into the collinear phase with larger moment when the external magnetic field increases. When the external field is reduced back to zero, the manganite does not regain the non-collinear phase. The collinear phase is metastable at low temperatures. The M versus H path is therefore not reversible at 5 K. This distinction in non-collinearity alone is not sufficient to explain the large difference in $H_{\text{int}}(0)$ in the two phases. A field as large as 535 kG shows that Fe is not highly covalent in this phase. A field of 470 kG, on the other hand, indicates that Fe is highly covalent in this phase. Earlier studies have indicated that the domain size of the two phases is of the order of several thousand Å. This is large enough to give magnetic spectra in Mössbauer spectroscopy. It is not clear why such a large domain did not contribute to the neutron diffraction peaks at 15 K.

5. Conclusions

We have observed phase separation above and below T_C . The two are independent and are related to different phenomena. The relative volumes of the two phases above and below T_C are also very different. Above T_C , the phase splitting is due to different lattice distortions. In one of the phases, Jahn–Teller distortion is significant. This Jahn–Teller distortion disappears when the temperature is lowered to T_C . The phase splitting below T_C is due to a difference in the nature of magnetic ordering and the degree of covalence of the magnetic ions in the two phases. The environment in one of the two phases is negligibly covalent and in the other highly covalent. The spin ordering in the two phases is collinear and non-collinear, respectively. At low temperatures, the non-collinear phase converts into the collinear phase when the applied magnetic field increases. The collinear phase is metastable. Mössbauer spectral shapes show large hyperfine magnetic field variation in the metallic state and negligible variation in the insulating phase.

References

- [1] Dagotto E, Hotta T and Moreo A 2001 *Phys. Rep.* **344** 1
- [2] Ramirez A P 1997 *J. Phys.: Condens. Matter* **9** 8199
- [3] Coey J M D, Viret M and von Molnar S 1999 *Adv. Phys.* **48** 167
- [4] Kusters R M, Singleton J, Keen D A, McGreevy R and Hayes W 1989 *Physica B* **155** 362
- [5] Von Helmolt R, Wecker J, Holzapfel B, Schultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331
- [6] Moreo A, Yunoki S and Dagotto E 1999 *Science* **283** 2034
- [7] Moreo A, Mayr M, Feiguin A, Yunoki S and Dagotto E 2000 *Phys. Rev. Lett.* **84** 5568
- [8] Moser A, Takano K, Margulies D T, Albrecht M, Sonobe Y, Ikeda Y, Sun S and Fullerton E E 2000 *J. Phys. D: Appl. Phys.* **35** R157
- [9] Ramirez A P, Schiffer P, Cheong S-W, Chen C H, Bao W, Palstra T T M, Gammel P L, Bishop D J and Zegarski B 1996 *Phys. Rev. Lett.* **76** 3188
- [10] Cheong S-W and Hwang H Y 1999 *Contribution to Colossal Magnetoresistance Oxides (Monographs in Condensed Matter Science)* ed Y Tokura (London: Gordon and Breach)
- [11] v Zimmermann M, Hill J P, Gibbs D, Blume M, Casa D, Keimer B, Murakami Y, Tomioka Y and Tokura Y 1999 *Phys. Rev. Lett.* **83** 4872
- [12] Mori S, Chen C H and Cheong S-W 1998 *Nature* **392** 473
- [13] Rao C N R, Arulraj A, Cheetham A K and Raveau B 2000 *J. Phys.: Condens. Matter* **12** R83
- [14] Zener C 1951 *Phys. Rev.* **81** 440
- [15] Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675
- [16] De Gennes P G 1960 *Phys. Rev.* **118** 141
- [17] Millis A J, Shraiman B I and Muller R 1996 *Phys. Rev. Lett.* **77** 175
- [18] Mizokawa T, Khomskii D I and Sawatzky G A 2001 *Phys. Rev. B* **63** 24403
- [19] Hebert S, Maignan A, Martin C and Raveau B 2002 *Solid State Commun.* **121** 229
- [20] Hwang H Y, Cheong S-W, Radaelli P G, Marezio M and Batlogg B 1995 *Phys. Rev. Lett.* **75** 914
- [21] Terai T, Kakeshita T, Fukuda T, Saburi T, Takamoto N, Kindo K and Handa M 1998 *Phys. Rev. B* **58** 14908
- [22] Neumeier J J, Hundley M F, Thompson J D and Heffner R H 1995 *Phys. Rev. B* **52** R7006
- [23] Hwang H Y, Palstra T T M, Cheong S-W and Batlogg B 1995 *Phys. Rev. B* **52** 15046
- [24] Kawakami T, Nasu S, Sasaki T, Kuzushita K, Morimoto S, Endo S, Yamada T, Kawasaki S and Takano M 2002 *Phys. Rev. Lett.* **88** 37602
- [25] Medvedeva I V, Barner K, Rao G H, Hamad N, Bersenev Yu S and Sun J R 2000 *Physica B* **292** 250
- [26] Freitas R S, Ghivelder L, Levy P and Parisi F 2002 *Phys. Rev. B* **65** 104403
- [27] Gerashenko A, Furukawa Y, Kumagai K, Verkhovskii S, Mikhalev K and Yakubovskii A 2003 *Phys. Rev. B* **67** 184410
- [28] Levy P, Parisi F, Granja L, Indelicato E and Polla G 2002 *Phys. Rev. Lett.* **89** 137001
- [29] Yakubovskii A, Kumagai K, Furukawa Y, Babushkina N, Taldenkov A, Kaul A and Gorbenko O 2000 *Phys. Rev. B* **62** 5337
- [30] Yusuf S M, Ganguly R, Chakraborty K R, Mishra P K, Paranjpe S K, Yakhmi J V and Sahni V C 2001 *J. Alloys Compounds* **326** 89
- [31] Blasco J, de Teresa J M, Ibarra M R, Algarabel P A and Marquina C 1996 *J. Phys.: Condens. Matter* **8** 7427
- [32] De Teresa J M, Ritter C, Ibarra M R and Algarabel P A 1997 *Phys. Rev. B* **56** 3317
- [33] Cai J-W, Wang C, Shen B-G, Zhao J-G and Zhan W-S 1997 *Appl. Phys. Lett.* **71** 1727
- [34] Yusuf S M, Sahana M, Hegde M S, Dorr K and Muller K H 2000 *Phys. Rev. B* **62** 1118
- [35] Kundaliya D C, Vij R, Kulkarni R G, Tulapurkar A A, Pinto R, Malik S K and Yelon W B 2003 *J. Magn. Magn. Mater.* **264** 62
- [36] Hasanain S K, Nadeem M, Hussain Shah W, Akbar M J and Hasan M M 2000 *J. Phys.: Condens. Matter* **12** 9007
- [37] Yusuf S M 1999 *Solid State Phys. (India)* **42** 518
- [38] Bhargava S C, Morrish A H, Kunkel H and Li Z W 2000 *J. Phys.: Condens. Matter* **12** 9667
- [39] Bhargava S C 1998 *Phys. Rev. B* **58** 3240
- [40] Bhargava S C and Iyengar P K 1974 *J. Physique Coll.* **35** C6 669
- [41] Bhargava S C and Zeman N 1980 *Phys. Rev. B* **21** 1726
- [42] Bhargava S C and Zeman N 1980 *Phys. Rev. B* **21** 1717
- [43] Clauser M J 1971 *Phys. Rev. B* **11** 3748
- [44] Bhargava S C, Knudsen J E and Morup S 1979 *J. Phys. C: Solid State Phys.* **12** 2879
- [45] Bhargava S C 1983 *Advances in Mössbauer Spectroscopy* ed B V Thosar, P K Iyengar, J K Srivastava and S C Bhargava (Amsterdam: Elsevier)