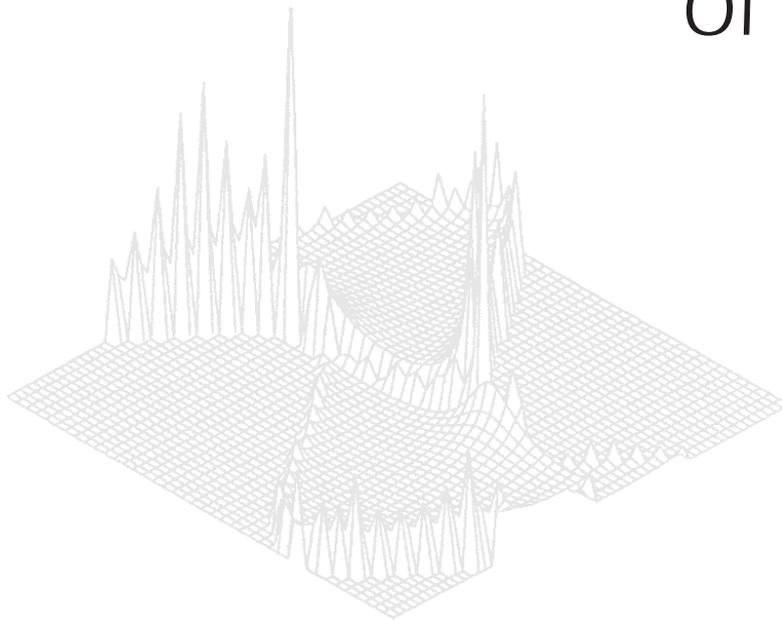

CSIRO PUBLISHING

Australian Journal of Physics

Volume 51, 1998
© CSIRO 1998



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^{57}Fe Mössbauer Experiments of Doped ($\text{La}_{0.67}\text{Ba}_{0.33}$)($\text{Mn}_{0.9}\text{Fe}_{0.1}$) O_3 *

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Abstract

We report on Mössbauer effect (ME) experiments on the compound ($\text{La}_{0.67}\text{Ba}_{0.33}$)($\text{Mn}_{0.9}\text{Fe}_{0.1}$) O_3 with the simple perovskite-like structure in the range from 4.2 to 300 K. From 190 to 300 K the spectra are described by a single quadrupole split doublet with a total splitting of $e^2qQ/2 = 0.38\text{ mm s}^{-1}$. This indicates that the local environment of the Fe^{3+} ions is not cubic, in contrast to the X-ray diffraction result on the same sample. At 4.2 and 25 K complex hyperfine (hf) split spectra are obtained. At least eight magnetically split subspectra with different hf fields must be used for describing these spectra adequately. From about 50 K up to 150 K the ME spectra reflect a relaxation process, indicating that the Fe moments fluctuate with frequencies in the range of the Larmor frequency in this temperature range. By describing the latter ME spectra by a magnetically split six-line spectrum with average hf fields and strongly broadened linewidths, the Fe moments are found to order below about 110 K. This value is much lower than the Curie temperature of $T_c = 190\text{ K}$ obtained from our magnetisation measurements. The fluctuations of the Fe moments observed down to low temperatures might be responsible for the fact that the metal–semiconducting transition, which usually occurs at T_c according to the double exchange model, is shifted from $T_c = 190\text{ K}$ down to 140 K.

1. Introduction

The perovskite manganites have recently received great interest because of the colossal magnetoresistance (CMR) effect. The undoped material LaMnO_3 orders antiferromagnetically (AF), just as LaCrO_3 and LaFeO_3 (Jonker 1956). By substituting Ba^{2+} on the La-sites ($\text{La}_{1-x}\text{Ba}_x$) MnO_3 becomes ferromagnetic (FM) and reaches its maximum value of $T_c = 340\text{ K}$ for $x = 0.33$ (Jonker and van Santen 1950). At the ferromagnetic transition temperature the transport properties change from insulating to a metallic-like behaviour, leading to a maximum resistivity at T_c . The magnetic and electric properties are coupled by Zener's (1951) double exchange (DE) model. Recently the magnetic and electric properties of ($\text{La}_{0.67}\text{Ba}_{0.33}$) MnO_3 have been investigated upon doping of Fe and Cr at the Mn sites by Osthöver and Arons (1998). For Cr doping T_c was found to decrease slightly from $T_c = 350$ to 310 K for 0.1 Cr. As expected from the DE model the temperature of the maximum resistance T_{MI} was found to coincide with T_c . From this it was concluded that the Cr–Mn coupling is FM. On the

* Refereed paper based on a contribution to the International Workshop on Nuclear Methods in Magnetism, held in Canberra on 21–23 July 1997.

other hand, T_c was found to be strongly reduced to $T_c = 190$ K upon 0.1 Fe doping at the Mn sites. This was ascribed to an antiferromagnetic (AF) coupling of the Fe to Mn moments. Additionally, the maximum resistivity appeared at much lower temperatures than T_c , i.e. at 140 K, in disagreement with the DE model. In order to understand these phenomena, we have investigated in the present work the ordering of the Fe moments by means of the Mössbauer effect.

2. Experimental Details

Mössbauer effect (ME) measurements on a polycrystalline sample of $(\text{La}_{0.67}\text{Ba}_{0.33})(\text{Mn}_{0.9}\text{Fe}_{0.1})\text{O}_3$ were performed at various temperatures of the absorber between 4.2 and 300 K. The γ -radiation source was $(^{57}\text{Co})\text{Rh}$ with an activity of about 10 mCi and was kept at 300 K for all measurements. The sample was not enriched by ^{57}Fe . Due to the small natural abundance of 2% ^{57}Fe only, the data acquisition time for the spectra ranged from 2 days at 300 K to one week at 4.2 K. Above 190 K the spectra could be analysed by one quadrupole doublet. For $T \leq 25$ K the superposition of a total of eight magnetically split six-line subspectra with Lorentzian line shape was necessary in order to fit the spectra adequately. In the temperature range $T = 48$ –153 K the spectra indicated a relaxation behaviour and were fitted using a simple Ising-type relaxation model.

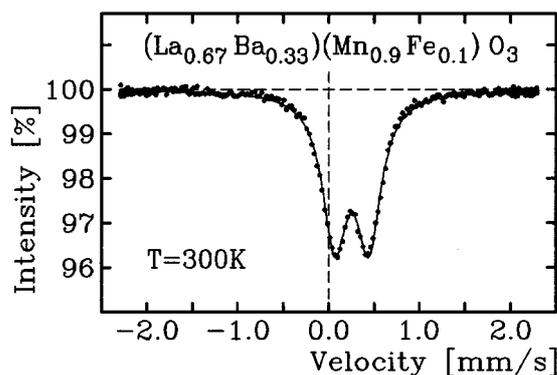


Fig. 1. The ^{57}Fe Mössbauer spectrum of $(\text{La}_{0.67}\text{Ba}_{0.33})(\text{Mn}_{0.9}\text{Fe}_{0.1})\text{O}_3$ at 300 K, showing the quadrupole split doublet due to the non-cubic environment of the Fe^{3+} ions.

3. Results and Discussion

Fig. 1 shows the ME spectrum of $(\text{La}_{0.67}\text{Ba}_{0.33})(\text{Mn}_{0.9}\text{Fe}_{0.1})\text{O}_3$ at room temperature. It has been fitted by one doublet with a total quadrupole splitting $\Delta E_Q = e^2qQ/2 = 0.38 \text{ mm s}^{-1}$ and an isomer shift (referred to $\alpha\text{-Fe}$) of $\text{IS} = +0.36 \text{ mm s}^{-1}$. This isomer shift value is compatible with Fe^{3+} . The existence of a quadrupole splitting indicates that the surrounding of the Fe atoms is not cubic in spite of the cubic perovskite structure obtained from the X-ray measurements. The cubic structure obtained from X-ray measurement on our sample agrees with the work on $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ by Jonker (1956), who concluded also that the phase becomes cubic for $x > 0.3$, while from neutron diffraction work by Elemans *et al.* (1971), in which the Ba concentration was only varied from $x = 0$ up to $x = 0.125$, the structure was found to be orthorhombic with

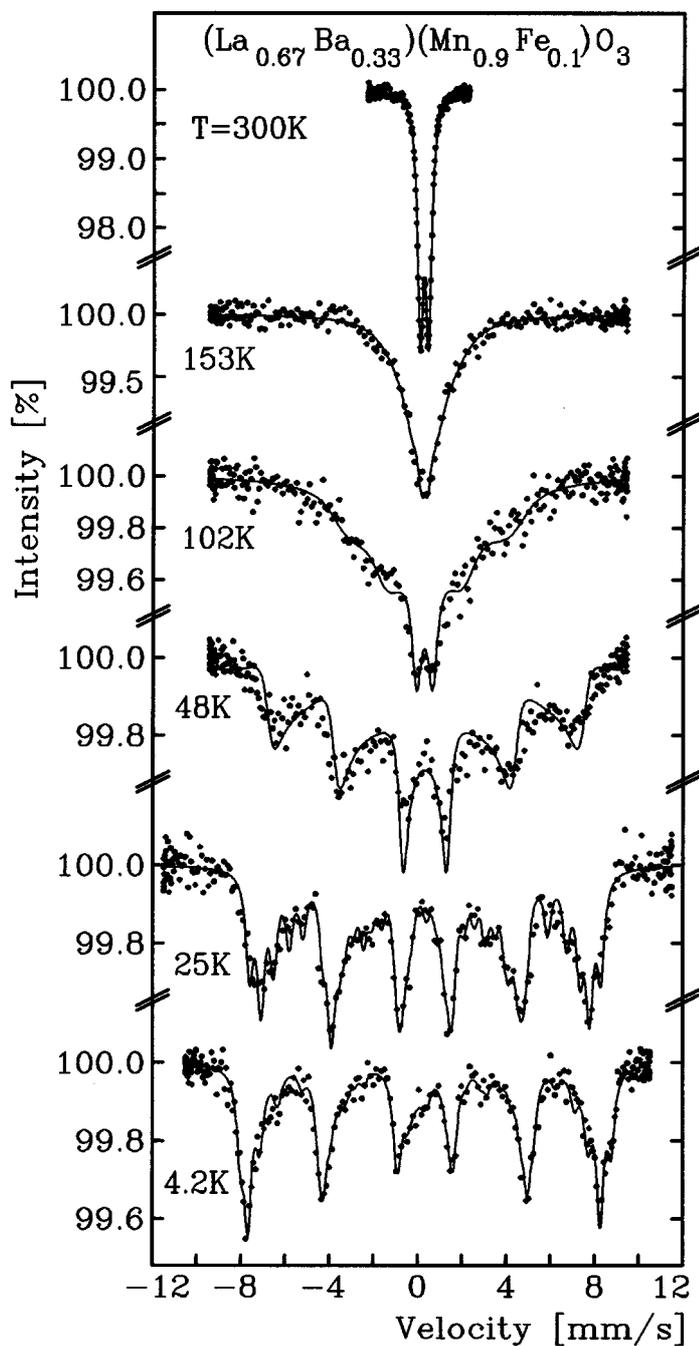


Fig. 2. The ^{57}Fe Mössbauer spectra of $(\text{La}_{0.67}\text{Ba}_{0.33})(\text{Mn}_{0.9}\text{Fe}_{0.1})\text{O}_3$ in the temperature range from 4.2 to 300 K. The spectrum at 300 K was already shown in Fig. 1 for a different velocity scale. Magnetically split six-line spectra are visible at 4.2 and 25 K. From about 50 to 150 K the spectra are characterised by a relaxation process.

space group $Pnma$. Accordingly, in view of our Ba content of $x = 0.33$, the cubic structure obtained by X-ray measurement is not surprising. Apparently, the distortion of the oxygen octahedra in this compound can only be detected by a local measurement like the ME.

On decreasing the temperature, the simple doublet spectrum starts to broaden near $T = 170$ K. At $T = 153$ and 102 K the overall shape of the spectra reflects a relaxation process (Fig. 2), indicating that the Fe moments fluctuate with a frequency in the range of the Larmor frequency of about 10^8 s⁻¹. Correspondingly, these two spectra could be fitted fairly well by assuming a simple Ising-type two-level relaxation model. The ME spectrum at 48 K still reveals these relaxation features. This spectrum could be fitted either by this relaxation model as plotted in Fig. 2 or, alternatively, by assuming a superposition of eight magnetically split subspectra. At lower temperatures (25 and 4.2 K) the spectra are quite complex and must be fitted by a superposition of at least eight magnetically split subspectra with different hyperfine (hf) field values. The isomer shift of these subspectra is still in the range of 0.35 – 0.45 mm s⁻¹ indicating that iron remains trivalent. The slight increase of the IS at low temperatures compared with room temperature can be explained by the second order Doppler shift.

While the observed Curie temperature of $T_c = 190$ K is caused by the ordering of the 90% Mn ions, apparently the 10% Fe ions order magnetically at lower temperatures, as follows from Fig. 2. The electronic configurations are $3d^5$ for Fe³⁺ and $3d^4$ and $3d^3$ for Mn³⁺ and Mn⁴⁺ respectively. In view of their half-filled 3d shell the Fe³⁺ ions can only couple antiferromagnetically to the (Mn³⁺, Mn⁴⁺) ions. Such an AF coupling explains the pronounced reduction of the Curie temperature of the Fe-doped compared with the Cr-doped compound, since Cr³⁺ is expected to couple ferromagnetically to the Mn sublattice. From the binomial distribution it is calculated that the probability of finding 0, 1 or 2 Fe ions on the six possible sites in the nearest neighbour (nn) shell around an Fe ion amounts to 53.1%, 35.4% and 9.8% respectively. The magnetic Fe³⁺–Fe³⁺ coupling, mediated by the usual super exchange via the intermediate oxygen ion, should be also antiferromagnetic (Goodenough 1966). Therefore, for the configurations with 1 or 2 Fe ions in the nn shell around an Fe ion there should arise a competition between the antiferromagnetic Fe–Fe and Fe–Mn couplings. This should lead to a frustration of the Fe ions depending on the number of the nn Fe ions. Probably, the low ordering temperature of the Fe moments at about 110 K, far below the Curie temperature of 190 K determined by the Mn moments, and the observed fluctuations of the Fe moments even down to about 50 K can be explained by this mechanism.

The different Fe–Mn neighbour configurations should reflect in individual subspectra with different hf fields due to the different transferred hf field contributions. Regarding exclusively the atoms in the nn shell around the Fe ions, three prominent subspectra with relative intensities of 53.1%, 35.4% and 9.8% would be expected. However, as mentioned above, at least eight subspectra are necessary for an adequate fit of the low-temperature spectra ($T \leq 48$ K). This suggests that also the next nn shell containing 12 atoms contributes to the hf fields.

At 4.2 K, i.e. near magnetic saturation, the subspectrum exhibiting the largest splitting corresponds to an hf field of 51.9 T. This is a value typically observed

for Fe oxides, i.e. non-metallic compounds. The existence of s-like conduction electrons would reduce the hf field by conduction electron polarisation to much lower values. Therefore, the present result is quite surprising because this compound shows metallic conductivity at low temperatures. Apparently, only the Mn ions are involved in the metallic conductivity.

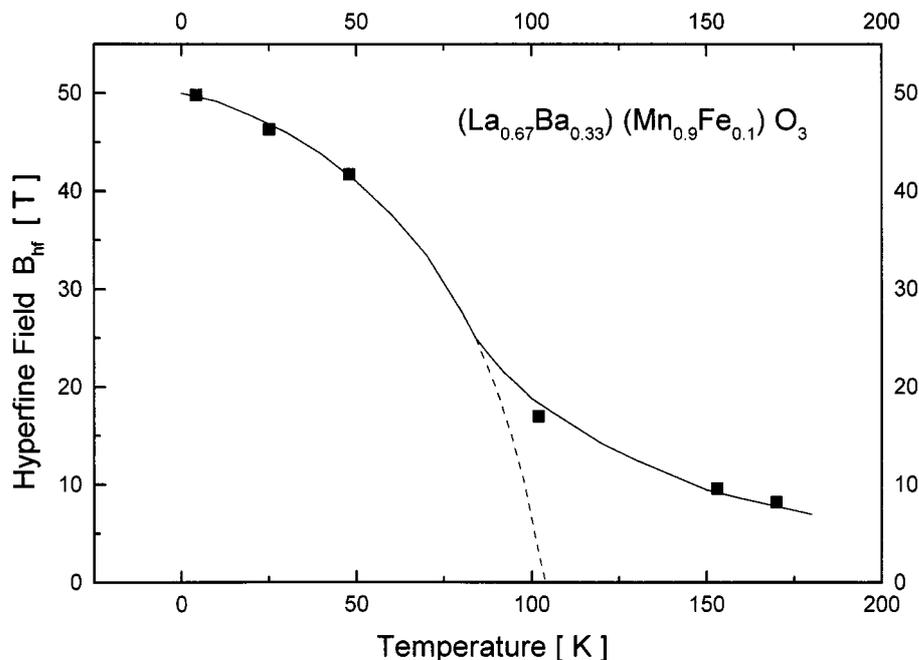


Fig. 3. Temperature dependence of the average hf field at the ⁵⁷Fe nuclei (see text). The dashed curve suggests an ordering of the Fe moments at about 110 K.

In a rough approximation one can fit the ME spectra below $T = 170$ K by only one magnetically split six-line spectrum with a strongly broadened linewidth in order to obtain an average value of the hf field as a function of temperature. The result is plotted in Fig. 3. This procedure is certainly inaccurate and therefore questionable due to the superimposed relaxation effects. But, nevertheless, the figure should provide roughly the data of the magnetisation curve of the Fe ions. As indicated by the dashed curve, there seems to be some kind of magnetic ‘ordering temperature’ around 110 K, while a tail in the magnetisation is retained nearly up to the Curie temperature of 190 K. At this moment it is not yet possible to conclude, whether this ‘ordering temperature’ is caused by the onset of an antiferromagnetic ordering or a canted spin structure of the Fe ions or that it has the character of a freezing temperature of the frustrated Fe moments.

4. Conclusions

The ferromagnetic ordering of $(La_{0.67}Ba_{0.33})MnO_3$ below the relatively high ordering temperature of $T_c = 350$ K is generally believed to be related to the

double exchange (DE) coupling between the Mn^{3+} and Mn^{4+} moments via the intermediate oxygen atoms (Zener 1951; Goodenough 1955, 1966). The magnetisation and resistivity measurements of Osthöver and Arons (1998) have shown that by 10% Cr doping at the Mn sites T_c is only slightly reduced to 310 K and that the maximum of the resistivity versus temperature curve, T_{MI} , coincides with T_c . Apparently, the DE coupling is only slightly modified by the introduction of Cr. From this, the Cr–Mn coupling is believed to be ferromagnetic (Osthöver and Arons 1998). On the other hand, in view of the half-filled 3d shell of the Fe^{3+} ions, the Fe–Mn coupling should be antiferromagnetic. Due to this, the ferromagnetic Mn–Mn ordering temperature is strongly reduced from 350 to 190 K for 10% Fe doping at the Mn sites (Osthöver and Arons 1998). Secondly T_{MI} was found to be located far below T_c , i.e. at about 140 K. From this, it was believed that the resistivity maximum in the Fe-doped compound was not only caused by the DE model, but additionally by the ordering of the Fe moments (Osthöver and Arons 1998). The present ME experiments confirm this hypothesis. While both the magnetisation measurements of Osthöver and Arons and the neutron diffraction experiments of Arons and Schäfer (1997) indicate that the Mn moments order FM below $T_c = 190$ K, the ME experiments show that the Fe moments order at much lower temperatures, i.e. at about 110 K, while even at temperatures as low as 50 K strong fluctuations of the Fe spin system are still observed.

The analogue system $(\text{La}_{0.7}\text{Pb}_{0.3})(\text{Mn}_{1-y}\text{Fe}_y)\text{O}_3$, with $0 \leq y \leq 0.17$, has been extensively investigated in the past (Leung *et al.* 1976). The ordering temperatures obtained by these authors from their magnetisation measurements agree roughly with the T_c values of Osthöver and Arons (1998). However, in contrast to our ME results the latter authors conclude from their ME experiments that, independent of the Fe-doping level, the Fe moments order at the same (high) temperature as the Mn moments (indicated by T_f in that work). In conclusion we can state that: *in $(\text{La}_{0.67}\text{Ba}_{0.33})(\text{Mn}_{0.9}\text{Fe}_{0.1})\text{O}_3$, the Mn and Fe moments order magnetically at very different temperatures.* The reason for this seems to be the strong AF coupling between two Fe^{3+} ions via the intermediate oxygen ions, which leads to frustration with respect to the AF coupling of Mn–Fe. In order to investigate this more carefully, further experiments on more diluted Fe-doping levels are in progress.

References

- Arons, R. R., and Schäfer, W. (1997). unpublished data.
 Elemans, J. B. A. A., van Laar, B., van der Veen, K. R., and Loopstra, B. O. (1971). *J. Solid State Chem.* **3**, 238.
 Goodenough, J. B. (1955). *Phys. Rev.* **100**, 564.
 Goodenough, J. B. (1966). 'Magnetism and the Chemical Bond' (Interscience: New York).
 Jonker, G. H. (1956). *Physica* **22**, 707.
 Jonker, G. H., and van Santen, J. H. (1950). *Physica* **16**, 337.
 Leung, L. K., Morrish, A. H., and Evans, B. J. (1976). *Phys. Rev. B* **13**, 4069.
 Osthöver, C., and Arons, R. R. (1998). Proceedings ICM' 97, Cairns; *J. Mag. Magn. Materials* **177–81** (in press).
 Zener, C. (1951). *Phys. Rev.* **82**, 403.