

Direct evidence of phase segregation and magnetic-field-induced structural transition in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ by neutron diffraction

C. Ritter

Institut Laue-Langevin, 38042 Grenoble Cedex, France

R. Mahendiran*

Departamento de Física de la Materia Condensada-ICMA, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain and Laboratoire CRISMAT, ISMRA, Université de Caen, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

M. R. Ibarra and L. Morellon

Departamento de Física de la Materia Condensada-ICMA, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

A. Maignan and B. Raveau

Laboratoire CRISMAT, ISMRA, Université de Caen, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

C. N. R. Rao

Solid State Structural Chemistry Unit, Indian Institute of Science, 560 012 Bangalore, India

(Received 28 December 1999)

We present direct evidence of the phase segregation and magnetic-field-induced structural transition in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ as proposed earlier [R. Mahendiran *et al.*, Phys. Rev. Lett. **82**, 2191 (1999)] for the collapse of the charge-ordered insulating state. The spontaneous ($H=0$) low-temperature phase at 125 K is found to be phase segregated into two different crystallographic structures and three magnetic phases: orthorhombic (*Imma*) ferromagnetic, orthorhombic (*Imma*) A-type antiferromagnetic, and monoclinic ($P2_1/m$) charge-ordered CE-type antiferromagnetic phases. Under a field of $H=6$ T, the charge-ordered monoclinic phase collapses and completely transforms into the metallic ferromagnetic orthorhombic phase.

It is now established that charge carriers doped into anti-ferromagnetic insulators such as nickelates and cuprates tend to group into some regions of the sample in the form of stripes at certain doping levels.¹ The electronic phase separation in the above compounds consists of arrays of doped holes interspaced with antiferromagnetic electron-rich regions. A different kind of electronic phase separation takes place in half-doped manganites such as $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, where doped e_g holes and e_g electrons are itinerant at high temperatures whereas they are localized at Mn^{+4} and Mn^{+3} sites, respectively, ordering in an alternate pattern below the charge ordering temperature T_{CO} . Such a charge ordering pattern was directly visualized by means of lattice imaging techniques in $R_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with $R=\text{La}$ (Ref. 2), Nd, Pr, Sm, etc.³ However, even for a small variation ($<3\%$) from the $\text{Mn}^{+3}:\text{Mn}^{+4}=50:50$ caused by either cation vacancies or oxygen off stoichiometry, a dramatic variation in the magnetic properties in terms of phase segregation into electron-rich ferromagnetic and electron poor antiferromagnetic domains can occur within the charge-ordered phase.⁴ This effect is likely to be more pronounced in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ since these compounds lie at the phase boundaries separating ferromagnetic and charge-ordered CE-type from non-charge-ordered A-type antiferromagnetic phases.⁵ Formation of ferromagnetic domains within a charge-ordered phase is inferred through low-field magnetization, magnetostriction,⁶ lattice imaging,² and nuclear-magnetic-resonance⁷ techniques. The onset of charge ordering in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is characterized by an abrupt jump in resistivity from a ferromagnetic metallic to an anti-ferromagnetic insulating state at $T_{\text{CO}}=148$ K while cooling.

Kuwahara *et al.*⁸ first observed several orders of magnitude of decrease in resistivity under a 7 T magnetic field and interpreted their results in terms of “melting” of the charge-ordered state under a magnetic field. However, the Zeeman energy gained under a 7 T magnetic field is incompatible with destroying the charge ordering and recently, based on a magnetostriction study in this compound, we have suggested⁶ that a magnetic-field-induced structural transition should take place in this compound. Such a field-induced-structural transition (FIST) was proposed to be facilitated by the coexistence of electronic and magnetic phase segregation with nearly comparable free energies. In this communication we report direct evidence of the proposed FIST by means of neutron diffraction. This is, to our knowledge, the first time that this technique has been utilized to probe a FIST in a manganite.

Powder neutron-diffraction data under $H=0$ T and 6 T were collected using the high-resolution instrument D2B at the Institute Laue-Langevin in Grenoble. The data were recorded from 10° to 160° (2θ) using a wavelength of $\lambda = 1.596$ Å. Rietveld analysis was done using the refinement program FULLPROF.⁹ Linear thermal expansion ($\Delta L/L$) under zero field was measured using the strain gauge method and the volume thermal expansion for the randomly oriented grains are obtained through the relation $\Delta V/V = 3\Delta L/L$. Our sample at the best can be described as $(\text{Nd}_{0.5}\text{Sr}_{0.5})_{1-x}\text{MnO}_3$ ($x \approx 0.03$) as refined through x-ray synchrotron and energy dispersive spectroscopic (EDS) analysis.⁴

Figure 1 serves as a guideline to the rest of the paper. As the temperature decreases from 300 K, volume thermal expansion data show a small hump around 270 K, and a more

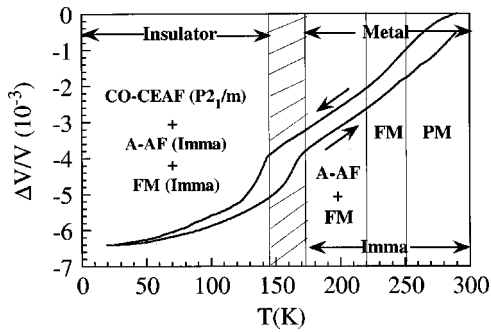


FIG. 1. Thermal dependence of the volume thermal expansion and phase diagram: PM (paramagnet), FM (ferromagnet), A-AF (A-type antiferromagnet), CO-CEAF (charge-ordered CE-type antiferromagnet). The structural space groups are also indicated.

pronounced drop ($\approx 0.12\%$) in the temperature range 147–125 K. While warming from 20 K, a rapid increase in volume occurs in the 160–175 K temperature interval and the feature around 270 K is more blurred. The magnitude of $\Delta V/V$ while warming at any given T is always lower than while cooling resulting in a hysteretic behavior up to room temperature. The above changes in volume are closely related to the intrinsic magnetic and electrical properties of the sample as indicated in the graph. The magnetic phases were identified from the earlier neutron and high-resolution synchrotron work of Woodward *et al.*⁴ The sample at 300 K in the paramagnetic phase is orthorhombic (*Imma*). As the temperature is decreased, first, A-type antiferromagnetic (A-AF) ordering with $d_x^2-d_y^2$ orbital ordering sets in at 220 K with distinct changes in the lattice parameters but without changing the *Imma* symmetry. Then, at 145 K, a charge-ordered phase with CE-type antiferromagnetic (CO-CEAF) ordering with d_z^2 orbital ordering develops with a monoclinic ($P2_1/m$) structure. The prominent drop in $\Delta V/V$ starting around 145 K is thus related to the *Imma*- $P2_1/m$ structural transition and the concomitant onset of charge ordering. However, both A-AF and FM phases were also found to coexist with CO-CEAF down to the lowest temperature (15 K) measured.⁴ Thus, the low-temperature phase is magnetically and structurally heterogeneous but when the sample is warmed up, only the *Imma* structure is found at 300 K. The observed hysteresis persisting up to high temperature is totally reproducible and might have its origin in an induced anisotropic strain and twinning by the orbital ordering at T_{CO} and T_{AF} resembling a martensitic transformation. It should be mentioned that a similar contraction of volume accompanying charge ordering and orthorhombic-monoclinic transition with hysteresis in $\Delta V/V$ up to 300 K are also observed¹⁰ in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, which has $T_{CO} < T_C$ as in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, but not in $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ or $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ where charge ordering occurs in the paramagnetic state and a small increase in volume around T_{CO} was found. It is also to be noted that while both $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($T_{CO} < T_C$) show positive volume magnetostriction,^{6,10} compounds with $T_{CO} > T_N$ show negative volume magnetostriction.^{11,12} The effect of oxygen isotope is as well different.¹³ Perhaps such different magnetovolume effects are one of the fundamental aspects of compounds with $T_{CO} < T_C$ and $T_{CO} > T_N$ but further studies are clearly needed. It should be mentioned that the earlier

work of Kuwahara *et al.*⁸ did neither suggest the coexistence of multiple magnetic nor of structural phases.

In Fig. 2 we show the powder neutron-diffraction pattern at 125 K under zero field [(a) and (c)] and under $H=6$ T. Our choice of this particular temperature (125 K) is due to the fact that we should be able to observe the FIST (see Fig. 1 in Ref. 6) within the maximum available field of 6 T in this experiment. The nuclear Bragg peaks and magnetic peaks are marked in graph. We find three magnetic phases, the majority being monoclinic CO-CEAF ($\approx 59.4\%$), orthorhombic A-AF ($\approx 21.6\%$), and orthorhombic FM ($\approx 19\%$). These phase fractions are also schematically depicted in Fig. 3(a). However, under $H=6$ T [Fig. 2(b)] both nuclear and magnetic peaks corresponding to the CE-COAF phase have completely vanished, the intensity of the A phase has decreased, and that of the FM phase increased. For the sake of clarity, a detail of the angular range $2\theta = 10^\circ - 35^\circ$ at 0 T (c) and 6 T (d) is shown. This is also schematically represented in Fig. 3(b) with the corresponding changes in magnetic moments shown in Fig. 3(c) and (d). The two different values of magnetic moment in the CO-CEAF phase in Fig. 3(c) are due to the fact that there exists two distinguishable sites for Mn ions (Mn^{+3} , Mn^{+4}) in the charge-ordered phase. The above results unequivocally support the collapse of the charge-ordered state through $P2_1/m$ to *Imma* (FM) and *Imma* (A-AF) to *Imma* (FM) transitions under a magnetic field as proposed earlier.⁶

No theoretical attempts have been made so far to explain the FIST phenomena in manganites. An experimental study of FIST was reported¹⁴ in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.17$) which undergoes first a rhombohedral to orthorhombic structural transition at 283 K, followed by ferromagnetic order ($T_C \approx 264$ K). The structural transition in this compound is driven by the cooperative Jahn-Teller distortion of Mn^{+3}O_6 octahedra. The low-temperature ferromagnetic orthorhombic phase at 240 K was suggested to undergo a reversible structural transition under magnetic field into a rhombohedral phase based on magnetostriction data.¹⁴ The transition was explained based on the phenomenological Landau theory of phase transitions involving two order parameters, magnetization (M) and lattice distortion (Q). However, our system is more complicated and involves a minimum of five order parameters and coupling between them: wave vector \mathbf{q} corresponding to charge order, Q_A and Q_{CE} corresponding to Jahn-Teller distortions involving $d_x^2-d_y^2$ and d_z^2 orbital ordering, uniform magnetization (M) of the ferromagnetic phase and two staggered magnetizations of M_{SA} and M_{SCE} corresponding to A- and CE-type antiferromagnetic ordering. A simplest case of coupled magnetic (para-ferro) and first-order structural transition (B31-B8₁) was reported in MnAs (Ref. 15) and explained through the Landau formalism.¹⁶ Recently, Michael van Veenendal and Fedro¹⁷ attempted to explain the ferromagnetic metal charge-ordered insulator transition invoking Jahn-Teller distortion and finite Coulomb interaction between electrons in the twofold degenerate e_g orbitals. According to them, the resistivity jump at the charge ordering temperature is caused by the narrowing of polaronic bandwidth and the formation of localized $3z^2-r^2$ polaron. While this model qualitatively explains the general trend of the observed resistivity behavior, it assumes an homogeneous charge-ordered phase in contrast to our experimental

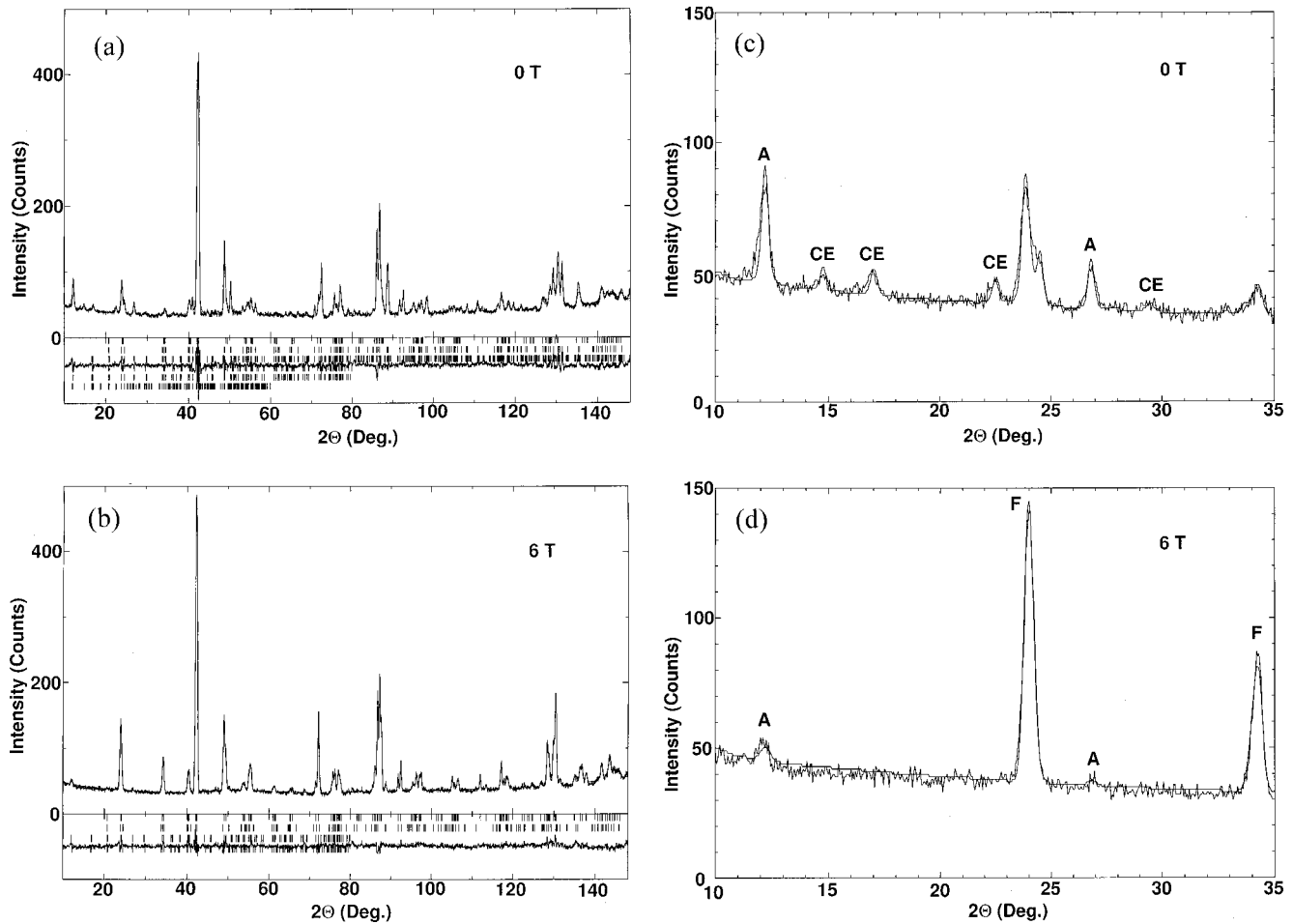


FIG. 2. Neutron powder diffraction pattern under $H=0$ T (a) and 6 T (b) at 125 K. The solid line is the Rietveld calculated profile. Allowed Bragg and magnetic reflections are indicated (tick marks) together with the residuals. A detail of the angular range $2\theta = 10^\circ - 35^\circ$ at 0 T (c) and 6 T (d) is included for the sake of clarity.

finding and does not consider the structural effects either. In spite of the absence of proper theoretical models, we can qualitatively understand our results in the following way. The free energy of the system can be written as $F = F_Z + F_{el} + F_{me} + F_{co}$, where the subscript stands for Zeeman,

elastic, magnetoelastic, and charge ordering. In zero field, all the three magnetic phases are degenerate in energy or differ only by small values. The mobility of e_g electrons under an external magnetic field can be enhanced in the orthorhombic structure rather than in the monoclinic due to the smaller degree of lattice distortion in the former. Hence, as the t_{2g} spins tend to align in the direction of the external magnetic field, the minimization of the free energy will favor a monoclinic to orthorhombic structural transition.

In conclusion, we have confirmed the phase segregation scenario in the charge-ordered compound $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and have shown the direct evidence for the magnetic-field induced monoclinic-orthorhombic structural transition and concomitant collapse of charge ordering in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. We have also found recently that a similar field induced structural transition (FIST) is the origin of CMR in the charge ordered $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$,¹⁰ electron doped compound $\text{Ca}_{0.85}\text{Sm}_{0.15}\text{MnO}_3$ and in A -type antiferromagnetic $\text{Pr}_{0.46}\text{Sr}_{0.54}\text{MnO}_3$.¹⁸ While our study opens up the possibility of looking out for the materials with CMR properties based on the FIST effect, a quantitative understanding remains an open problem.

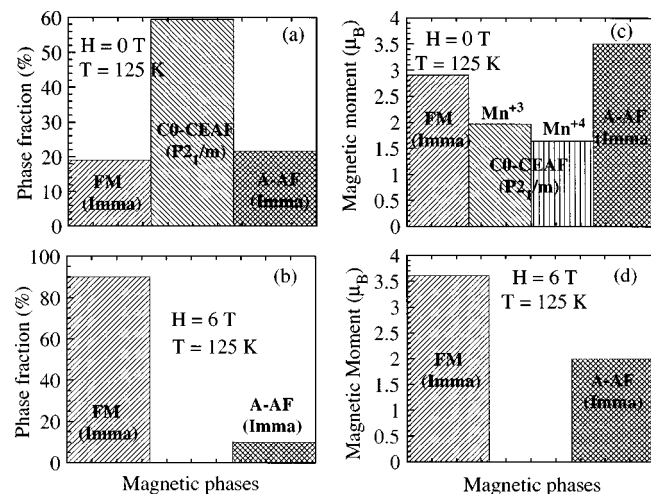


FIG. 3. Schematic diagram of percentage volume fraction under $H=0$ T (a) and 6 T (b) and magnetic moment values under $H=0$ T (c) and $H=6$ T (d).

R.M. thanks MENRT (France) and Ministerio de Educacion Y Cultura (Spain) for financial help, and A. Arulraj for providing the sample.

- * Author to whom correspondence should be addressed. Electronic address: mahendiran.mahi@ismra.fr
- ¹J. M. Tranquada *et al.*, Phys. Rev. Lett. **79**, 2133 (1997); Nature (London) **375**, 561 (1995).
- ²S. Mori, C. H. Chen, and S. W. Cheong, Phys. Rev. Lett. **81**, 3972 (1998).
- ³A. Barnabé, M. Hervieu, A. Maignan, C. Martin, and B. Raveau, J. Appl. Phys. **84**, 5506 (1998).
- ⁴P. M. Woodward, T. Vogt, D. E. Cox, C. N. R. Rao, and A. K. Cheetham, Chem. Mater. **11**, 3528 (1999).
- ⁵A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).
- ⁶R. Mahendiran, M. R. Ibarra, A. Maignan, F. Millange, A. Arulraj, R. Mahesh, B. Raveau, and C. N. R. Rao, Phys. Rev. Lett. **82**, 2191 (1999).
- ⁷G. Allodi, R. De Renzi, F. Licci, and M. W. Pieper, Phys. Rev. Lett. **81**, 4736 (1999).
- ⁸H. Kuwahara, Y. Tomioka, and Y. Tokura, Science **270**, 961 (1995); H. Kawano, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **78**, 4253 (1997).
- ⁹J. Rodriguez-Carvajal, Physica B **192**, 55 (1993).
- ¹⁰R. Mahendiran, M. R. Ibarra, A. Maignan, C. Martin, B. Raveau, and A. Hernando, Solid State Commun. **111**, 525 (1999).
- ¹¹R. Mahendiran, C. Marquina, M. R. Ibarra, A. Maignan, B. Raveau, and C. N. R. Rao (unpublished).
- ¹²J. M. De Teresa, M. R. Ibarra, C. Marquina, P. A. Algarabel, and S. Oseroff, Phys. Rev. B **54**, R12 689 (1997).
- ¹³R. Mahesh and M. Itoh, J. Solid State Chem. **144**, 232 (1999); G. Zhao *et al.*, Phys. Rev. B **59**, 81 (1999).
- ¹⁴A. Asamitsu, Y. Moritomo, R. Kumai, and Y. Tokura, Phys. Rev. B **54**, 1716 (1996).
- ¹⁵C. P. Bean and D. S. Rodbell, Phys. Rev. **126**, 104 (1962); V. A. Chernenko, L. Wee, P. G. McCormick, and R. Street, J. Appl. Phys. **85**, 7833 (1999).
- ¹⁶J. C. Tolédano and P. Tolédano, *Landau Theory of Phase Transition* (World Scientific, Singapore, 1987), Chap. VI and references therein.
- ¹⁷Michael van Veenendal and A. J. Fedro, Phys. Rev. B **59**, 15 056 (1999).
- ¹⁸R. Mahendiran, M. R. Ibarra, A. Maignan, C. Martin, B. Raveau, and C. Ritter (unpublished).