

Structural Instability of the Charge Ordered Compound $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ under a Magnetic Field

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We report an anomalous magnetostriction behavior of the charge ordered compound $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. We have found that the applied magnetic field not only gives rise to a large negative magnetoresistance but also produces a huge positive magnetovolume effect. This unusual effect is explained considering that the applied magnetic field induces a structural transition at which the volume drastically increases. This effect is also seen in the anisotropic magnetostriction which shows clear anomalies at the field induced transition. [S0031-9007(99)08574-9]

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The manganates $R_{1-x}D_x\text{MnO}_3$ (where R and D are trivalent and divalent ions, respectively) exhibit many spectacular properties of which colossal magnetoresistance (CMR) is just one [1,2]. Ferromagnetism and metallicity coexist in these materials due to the double exchange mechanism [3]. Even though a clear understanding of the origin of CMR in these materials is yet to emerge, it is well accepted that the lattice distortion (due to the smaller A -site cations and Jahn-Teller distortion of Mn^{3+} ions) plays a major role in governing magnetoresistance and other properties [4–6]. An orthorhombic distortion resulting from an ordering of the filled e_g : d_z^2 or $d_x^2-d_y^2$ orbitals can localize the charge carriers, leading to a collapse of the ferromagnetic metallic state. For example, $d_x^2-d_y^2$ orbital ordering below 140 K in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ leads to the confinement of the e_g electron within two dimensional MnO_2 planes and A -type antiferromagnetism [7]. In $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, d_z^2 orbital ordering below 150 K leads to an insulating state with CE -type antiferromagnetic order [7]. The Coulomb repulsion among the carriers localized at d_z^2 orbitals results in charge ordering (i.e., the ordering of e_g electron and hole in the Mn^{3+} and Mn^{4+} sublattice, respectively). Recent tunneling spectroscopy experiments on $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ showed that a gap of ≈ 0.3 eV opens up in the density of states at the charge ordering temperature [8]. This gap is much larger than the charge ordering temperature ($= 12$ meV) and it is not clear how a magnetic field of a few teslas ($= 1.2$ meV at 6 T) can destroy the charge ordered state. In order to understand this effect which involves so different energy scales we undertook magnetostriction studies in $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.5, 0.55$) systems. In recent times the magnetostriction technique has emerged to be an invaluable experimental tool to underscore the strength of the electron-lattice interaction and the existence of phase separation in manganates [9].

Our samples $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.5, 0.55$) have been characterized by different techniques. These results have been reported elsewhere [10,11]. The resistivity (ρ) of the $x = 0.5$ sample with the T_c of 248 K undergoes a ferromagnetic metal-antiferromagnetic charge ordered (C.O.) insulator transition at 140 K. The $x = 0.55$ sample shows A -type ordering at 220 K and a small kink in resistivity around 220 K but remains insulating down to 4.2 K ($\rho_{4.2\text{K}} = 0.2 \Omega \text{ cm}$). The maximum magnetoresistance in this sample occurs around 200 K and a spontaneous structural transition takes place in the zero field around 225 K [7]. Magnetization up to 12 T was measured with a superconducting coil in a vibrating-sample magnetometer apparatus up to 12 T. Magnetostriction measurements were carried out using the strain gauge technique under pulsed field up to 13.7 T in parallel and perpendicular configurations. The volume and anisotropic magnetostriction are obtained as $\omega = \lambda_{\parallel} + 2\lambda_{\perp}$ and $\lambda_t = \lambda_{\parallel} - \lambda_{\perp}$, respectively, where λ_{\parallel} and λ_{\perp} stand for the magnetostriction measured parallel and perpendicular to the field.

In Fig. 1 we show the field dependence of volume magnetostriction (right panel) in the $x = 0.5$ sample at selected temperatures. For the sake of clarity magnetization isotherms are also reported in the left panel of this figure. The sample is ferromagnetic between 250 and 150 K and the magnetization even in a field as high as 12 T is less than the theoretical value of $3.5\mu_B$. This is an important observation to be noted as this suggests that the ferromagnetic metallic phase does not extend to the whole sample as will be discussed later. The low temperature data ($T < 150$ K) in the bottom left panel shows that the sample undergoes an antiferromagnetic to a ferromagnetic transition at a certain critical field H_c [which can be identified as field corresponding to maximum slope of high field $M(H)$ curve]. H_c increases as the temperature is reduced in close agreement with the earlier report in Ref. [7]. The small increase in magnetization at low field

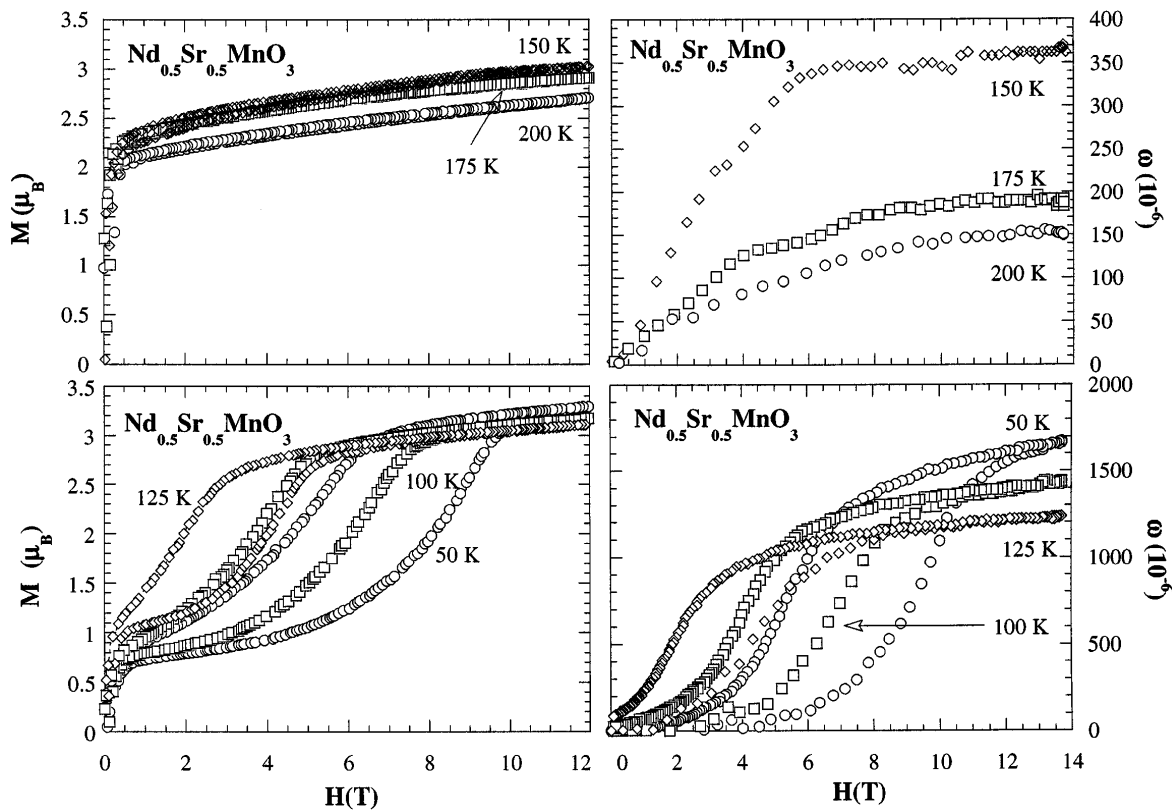


FIG. 1. Left panels: Field dependence of magnetization of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ in the ferromagnetic state (top) and charge ordered antiferromagnetic state (bottom). Right panels: Field dependence of volume magnetostriction (ω) in the ferromagnetic state (top) and in the charge ordered antiferromagnetic state (bottom).

may reflect the presence of ferromagnetic regions in the charge ordered state as will be discussed later. The right panel of Fig. 1 shows that the magnitude of volume magnetostriction (ω) increases with increasing field strength and decreasing temperature. In the charge ordered state ($T < 150$ K), ω is small up to a critical field H_c at which a rapid increase occurs which is consistent with the magnetization behavior. ω at 13.7 T is as high as 0.17%. This is the *first evidence* of an increase of volume under applied magnetic field in a charge ordered manganate. This rather unusual behavior gives valuable information in order to understand the ground state of this system in the whole range of temperature.

Figure 2 shows the anisotropic magnetostriction (λ_t) at few selected temperatures. In the metallic state (250–150 K), λ_t shows a sharp raise at low field as expected for a ferromagnet during the domain wall displacement process. In a soft ferromagnet λ_t saturates once this process is completed [12]. In contrast to this we see that the high field λ_t decreases with the field (more clearly visible for 150 K data). This suggests that the high field process (paraprocess regime) is dominated by some other mechanism. The λ_t of $x = 0.55$ is less than 0.01% over a wide temperature range.

The above results are clearly shown in Fig. 3 where ω at 13.7 T is plotted as a function of temperature. ω for $x = 0.5$ is positive over a wide temperature range and

shows a sharp increase below T_{co} . In contrast, it is negligible in $x = 0.55$ over the whole range of temperature except around 200 K. The lack of appreciable volume effect in $x = 0.55$ is due to the need of fields larger than 14 T to destroy the antiferromagnetic order which is beyond our experimental limits (see the magnetization curve in the inset).

Now we try to explain the origin of the large and positive value of the magnetovolume effect. It is now widely accepted [5,9] that the insulator-metal transition in manganates is accompanied by a huge spontaneous volume contraction of $\approx 0.1\%$. The origin of this effect has been attributed [13] to the delocalization of charge carriers which are localized as magnetic polarons in the paramagnetic insulating state. A similar effect is also found under the magnetic field at temperatures above T_c [10,13]. The destruction of the charge ordered state in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ also gives rise to a large negative magneto volume ($\approx 0.12\% - 0.14\%$) and negative magnetoresistance [9,14]. The destruction of charge ordering in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ by a magnetic field leads to nearly 100% negative magnetoresistance and one would have expected a *volume contraction* of $\approx 0.15\%$ based on the result of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. The present observation of *volume expansion* of $\approx 0.17\%$ at 50 K and 13.7 T is rather unusual and against our expectations. Then, we should reconsider the low temperature ground state and the field effect in

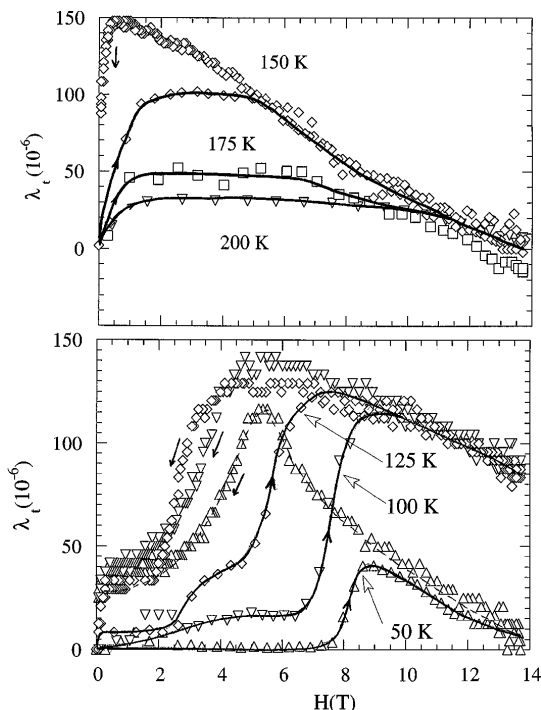


FIG. 2. Anisotropic magnetostriction (λ_t) of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ in the ferromagnetic state (top) and charge ordered state (bottom). Note that the high field λ_t decreases with increasing field.

terms of mechanisms other than based on carrier mobility alone. Recent synchrotron and neutron diffraction studies of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ [11] show that the room temperature phase is orthorhombic (*Imma*) and the paramagnetic-ferromagnetic transition at 248 K is smooth and does not imply any volume change. However, below 220 K (i.e., in the metallic state) the coexistence of an A-type antiferromagnetic (AF) with a $d_x^2-d_y^2$ orbital ordering occurs. In this phase also the point symmetry is kept but a volume contraction of the unit cell takes place [11]. Below 150 K, the C.O. transition is accompanied by d_z^2

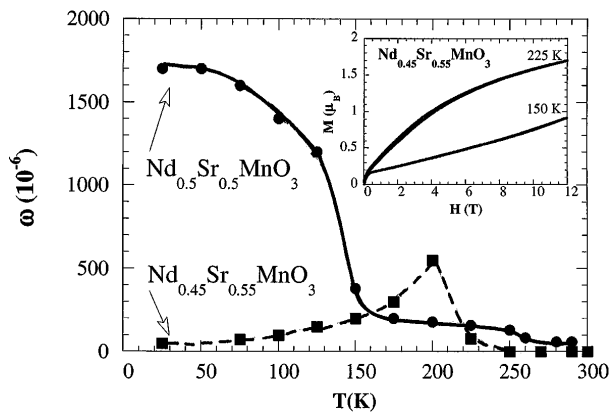


FIG. 3. The temperature dependence of the maximum volume magnetostriction at the $H = 13.7$ T for $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.5, 0.55$) samples. The inset shows the field dependence of magnetization for the $x = 0.55$ sample. Note that there is no metamagnetic transition up to 12 T.

orbital ordering, but this transition is also inhomogeneous and the symmetry changes to monoclinic ($P2_1/m$ space group). The ground state at low temperature is proposed as phase segregated in which three phases with different unit cell volumes coexist [11]. The unit cell volume of the remaining orthorhombic ferromagnetic high temperature phase is $V_{\text{HTO}} = 159.4 \text{ \AA}^3$. The lowest volume phase is the $d_x^2-d_y^2$ orbital ordered A-type AF ($V_{\text{LTO}} = 158.65 \text{ \AA}^3$). The majority phase, i.e., the C.O. monoclinic CE-type AF has a unit cell volume of $V_{\text{LTM}} = 159.1 \text{ \AA}^3$. Having in mind the delicate energy balance among different interactions which interplay in this system, we can consider that the small energy contribution supplied by the applied magnetic field is sufficient to destroy this metastable low temperature ground state. We propose that at a high enough field the system transforms into a homogeneous state which may be related to the high temperature ferromagnetic state with a volume unit cell of V_{HTO} . This assumption implies a volume change as a consequence of the transformation of the C.O. monoclinic CE-type AF and the orthorhombic A-type AF into the ferromagnetic phase.

It should be noted that this transformation is favorable because the charge carriers can gain more kinetic energy in the high temperature *Imma* phase which do not allow Jahn-Teller distortion [10]. We have estimated the volume change associated with this transition by obtaining the average unit cell volume as $\langle V \rangle = n_F V_{\text{HTO}} + n_{\text{A-AF}} V_{\text{LTO}} + n_{\text{CE-AF}} V_{\text{LTM}}$, where n_F , $n_{\text{A-AF}}$, and $n_{\text{CE-AF}}$ stand for the fractions of the coexisting phases in the absence of applied magnetic field. If we assume a phase percentage as in Ref. [12] ($n_{\text{CE-AF}} = 0.6, n_{\text{A-AF}} \approx n_F = 0.2$) $\langle V \rangle = 159.07 \text{ \AA}^3$ and the calculated volume magnetostriction: $\omega = [V(14 \text{ T}) - V(0 \text{ T})]/V(0 \text{ T}) = (V_{\text{HTO}} - \langle V \rangle)/\langle V \rangle = 2.0 \times 10^{-3}$. This value agrees not only qualitatively but also quantitatively with the measured volume magnetostriction ($\omega = 1.7 \times 10^{-3}$ at 13.7 T and 50 K). As a result the observed volume effect supports the existence of spontaneous electron phase segregation at low temperatures in this system which can be reversed by an applied magnetic field. This magnetic field induced structural transition differs from the earlier report [15] on $\text{La}_{0.83}\text{Sr}_{0.17}\text{MnO}_3$ where the transition is from high volume orthorhombic to low volume rhombohedral structure, and the magnetic field has an effect on this transition only in a very narrow temperature range.

The lack of space in this Letter does not allow us to describe the anisotropic magnetostriction in detail. But we emphasize that λ_t do indeed reflect the transformation of the various magnetic phases as field evolves. For example, the 125 K data [see Fig. 2 (bottom)] shows a small but clearly visible raise of λ_t at low field (contribution from FM micro regions) and another raise around 2 T (transformation of the A-type phase) and finally one more raise around 5 T (as the remaining CE-type phase transforms into the FM phase). The

decrease of λ_t at higher fields may be the consequence of the field induced structural transition. The lack of saturation of magnetostriction and magnetization further confirms the inhomogeneous ferromagnetic metallic state as revealed by the neutron results [11].

Unlike many theoretical works [16] which neglect lattice effects and attribute C.O. due to Coulomb repulsion alone, the present observation underscores the presence of a strong coupling between elastic, magnetic, and Coulomb energies. Magnetic field induced structural transitions are very rare in condensed matter physics, and the present results suggest that elastic modulus of these compounds are very much sensitive to magnetic field. When C.O. arises out of the FM metallic state as in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, it seems that the applied magnetic field simultaneously induces structural transition and melts charge order. But when the C.O. arises out of the paramagnetic state as in $(\text{Pr}, \text{Nd})_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ or $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, the applied magnetic field while partially melting the charge order reduces local distortion without changing the structure. The difference between both these cases also have been beautifully illustrated by the isotopic effect: while the O^{18} isotope does not have a major influence $T_{\text{C.O.}}$ in $(\text{La}, \text{Nd})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [9] and $(\text{Pr}, \text{Nd})_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [17], $T_{\text{C.O.}}$ is shifted up by 21 K in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and 16 K in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [17].

In conclusion, for the first time we have observed an unexpected huge positive magnetovolume effect over a wider temperature range in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ while the magnetoresistance is still negative. The observed effect is due to the field induced structural transition. The applied magnetic field has a different effect on the charge ordered state depending on whether C.O. is established in the paramagnetic state or in the ferromagnetic state. Further investigations such as elastic modulus and neutron diffraction under magnetic field may provide further information.

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