Internal friction study on the phase separation behaviour in La$_{0.8}$Ca$_{0.2}$MnO$_3$

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Abstract

The ferromagnetic (FM) manganite $La_{0.8}Ca_{0.2}MnO_3$ is systematically studied by measurements of internal friction Q^{-1}, Young's modulus E, resistivity ρ and magnetization M versus temperature T. The resistivity $\rho(T)$ exhibits a metal–insulator transition (MIT) at $T_p \sim 224$ K. The magnetization $M(T)$ shows a paramagnetic–ferromagnetic (PM–FM) transition at $T_c \sim 240$ K and saturates around 182 K. However, the variation of the internal friction with temperature presents a complicated behaviour. In the FM region, three Q^{-1} peaks at temperatures 98, 143 and 163 K are observed in the spectra of $Q^{-1}(T)$ at the measuring frequency of 1.8 kHz. The origin of three Q^{-1} peaks is discussed and attributed to the coexistence of metallic and insulating phases in the FM region. In addition, in the magnetic transitional region, the other two peaks at 182 and 244 K at the measuring frequency of 1.8 kHz are observed. Our results indicate that the internal friction method seems to be a useful technique in studying the coupling between spin, charge and lattice of CMR materials.

1. Introduction

Since the colossal magnetoresistance (CMR) effect in perovskite manganese oxides $R_{1-x}A_xMnO_3$ (R is a trivalent rare-earth such as La, Nd, Pr, etc, A is a divalent dopant such as Ca, Sr, Ba, Pb, etc) was discovered, it has been extensively studied in past years because of its value in fundamental physics and its potential applications [1–3]. The basic mechanism for transport and magnetism in these oxides is believed to be double exchange (DE) [5] together with the Jahn–Teller (JT) effect [5–7]. These interactions with similar energy scales make

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the ground state of the system subtle. Evidence from theory [8] shows that spatial phase separation (PS) may occur between hole-rich (ferromagnetic metallic (FM)) and hole-poor (antiferromagnetic insulating) regions.

Experimentally, several papers have reported that the FM phase in $La_{1-x}Ca_xMnO_3$ which is a typical DE system has a complicated character [9, 10]. Fäth *et al* investigated $La_{1-x}Ca_xMnO_3$ single crystals and thin film with x of about 0.3 using scanning tunnelling spectroscopy (STS) and found a PS where inhomogeneous structures of metallic and insulating phases coexisted [9]. The coexistence of two FM phases was also observed by using ^{55}Mn NMR in $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ ferromagnetic manganites [10]. Other investigations of the ^{55}Mn NMR line shape of $La_{1-x}Ca_xMO_3$ suggest that in the doping range $0.2 \leqslant x \leqslant 0.5$ a mixed ferromagnetic state exists which is comprised of FM insulating and FM metallic regions [12]. Magnetization, ac susceptibility and neutron scattering studies also provide the evidence for the formation of two FM phases (metallic and insulting) in low-doped $La_{1-x}Ca_xMnO_3$.

From a mechanical point of view, these composites are also an inhomogeneous system due to the strong correlation among spin, charge and lattice. The electron localization and spin orientation are generally accompanied by lattice distortion [9]. If the deformation is inhomogeneous, the components with different lattice deformations have different mechanical properties which result in stress concentration, the propagation of lattice deformation and motion of boundaries among different components. The coupling between electron and lattice or spin and lattice is expected to be large enough to produce damping in the composite. The internal friction measuring technique is a nondestructive but very sensitive tool in studying defects and microscopic processes in solids including cuprate high temperature superconductors and manganites [13–16]. In this paper, we report the PS behaviour of $La_{0.8}Ca_{0.2}Mn_3$ by measurements of internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$ at a zero magnetic field. By means of internal friction measurements under different measuring frequencies, one may determine whether the microscopic process is phase transition or relaxation, and some other quantitative information such as activation energy and the relaxation time at infinite temperature can be obtained. In addition, the concomitant Young's modulus reflects the information of the lattice variation.

2. Experimental details

A polycrystalline $La_{0.8}Ca_{0.2}MnO_3$ sample was prepared by the standard solid state reaction. Stoichiometric mixtures of La_2O_3, $CaCO_3$ and MnO_2 powders were mixed and ground, and then calcined at 1000 and 1200 °C for 24 h several times with intermediate grinding. Finally, the material was sintered for 48 h with an intermediate regrinding, then furnace cooled to room temperature. X-ray powder diffraction was performed using a Philips X'pert PRO x-ray diffractometer with Cu Kα radiation at room temperature and was refined using a standard Rietveld technique. The resistivity of $La_{0.8}Ca_{0.2}MnO_3$ was measured by the conventional four-probe technique. The magnetic measurements were performed on a Quantum Design superconducting quantum interference device (SQUID) MPMS system ($2 \leqslant T \leqslant 400$ K, $0 \leqslant H \leqslant 5$ T). $Q^{-1}(T)$ and $E(T)$ were measured by the free decay method of a resonant bar made of $La_{0.8}Ca_{0.2}MnO_3$ in the acoustic frequency range with a magnitude of kilohertz and in the temperature range of 80–300 K using the warming mode in a helium gas environment at the rate of 0.3 K min^{-1} under zero applied magnetic field. The size of samples used in Q^{-1} and E measurements is $70 \times 4 \times 1.8$ mm^3. The sample was excited electromagnetically in the fundamental and the first free flexural modes, whose resonant frequencies f are in the ratios 1:2.76. The internal friction Q^{-1} is defined as follows [13]:
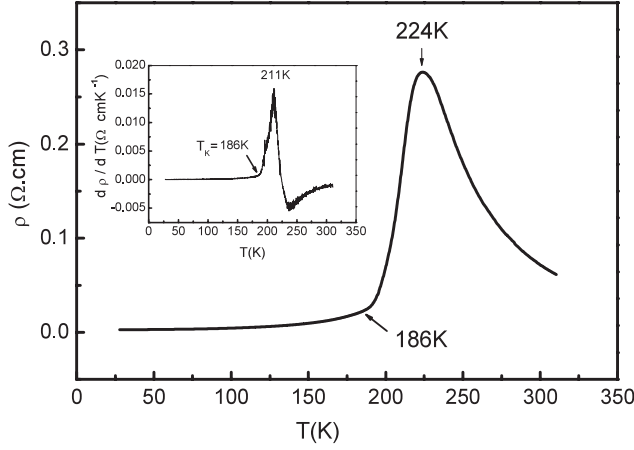
Figure 1. Temperature dependence of the resistivity for La$_{0.8}$Ca$_{0.2}$MnO$_3$ at zero magnetic field. The inset shows dρ/dT versus temperature, and T_K is defined as the temperature below T_P at which dρ/dT begins to rise rapidly.

$$Q^{-1} = \frac{1}{n} \ln\left(\frac{A_0}{A_n}\right), \tag{1}$$

where n is the number of the vibration cycles, while the amplitude attenuates from A_0 to A_n. The Young modulus E is given by

$$E = \frac{4\pi^2 s d l^4}{m^4 I} f^2, \tag{2}$$

where f is the resonant frequency, s is the cross-sectional area, d the density, l the length and I the moment of inertia of the sample. In addition, m is 4.730 for the vibrating mode in the fundamental mode, in which the sample is suspended at two points whose span is $0.224l$ from two free ends of the sample. We define the resonant frequency f in the fundamental mode at room temperature (300 K) as measuring frequency $f_0 = 1.80$ kHz, thus the measuring frequency in the first free flexural mode as $2.76f_0$, i.e. 4.97 kHz. Based on equation (2), E is proportional to the square of the resonant frequency, i.e., $E \propto f^2$. Therefore, we substitute f^2 for the Young modulus E. For the sake of convenience, the relative modulus is defined as $\Delta E = [f^2(T) - f_{min}^2]/[f_{max}^2 - f_{min}^2]$. Here, f_{min} and f_{max} are the minimum and maximum resonant frequencies in the whole measuring temperature range, respectively.

3. Results and discussion

Powder x-ray diffraction measurement at room temperature indicates that the investigated sample La$_{0.8}$Ca$_{0.2}$MnO$_3$ is single phase. All diffraction peaks can be indexed by an orthorhombic lattice with space group $Pbnm$ and lattice parameters of $a = 5.4961$ Å, $b = 5.4933$ Å and $c = 7.7701$ Å. The temperature dependence of resistivity $\rho(T)$ in La$_{0.8}$Ca$_{0.2}$MnO$_3$ is shown in the main panel of figure 1. A distinct MIT occurs at the temperature $T_p = 224$ K. The inset of figure 1 shows the differential of resistivity dρ/dT versus temperature, which exhibits a rapid rise around 186 K (denoted by T_K) with increasing temperature. Below T_K, dρ/dT of the sample seems to be independent to the temperature and without any detectable anomaly in it, which seems to imply that the sample lies in a homogeneous metallic state below T_K.

The temperature dependence of magnetization $M(T)$ at an applied field of $H = 0.01$ T in a field-cooled mode is given in the main panel of figure 2. It shows that the sample undergoes a PM–FM transition at Curie temperature $T_c = 240$ K, defined as the inflection point on the $M(T)$ curve. Furthermore, M varies slightly below 182 K, which implies that the sample seems to lie in a homogeneous FM state.
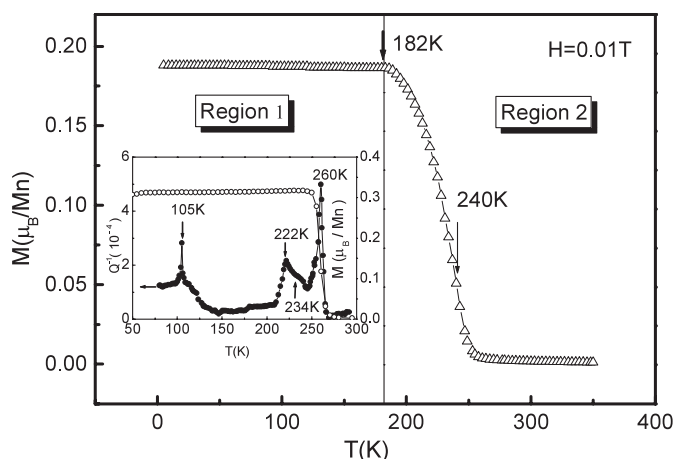
Figure 2. The main panel shows the temperature dependence of magnetization of $La_{0.8}Ca_{0.2}MnO_3$ under the field-cooled mode at an applied magnetic field of $H = 0.01$ T. The inset shows the temperature dependence of internal friction Q^{-1} at the measuring frequency of 2.56 kHz and magnetization M of $La_{0.67}Ca_{0.33}MnO_3$ at $H = 0.01$ T.

Combining the result of M with that of ρ, the magnetic and electrical behaviour of $La_{0.8}Ca_{0.2}MnO_3$ seems to be divided into two regions, which are separated by a solid line located at $T = 182$ K, as shown in figure 2: region 1 is the homogeneous FM metallic state below 182 K and region 2 is the magnetic transitional part accompanying the MIT in the temperature range of $T \geqslant 182$ K. To test whether this viewpoint is correct, both Q^{-1} and E are measured at different measuring frequencies of 1.80 and 4.97 kHz. The results are shown in figures 3 and 4. The internal friction in figure 3 exhibits five peaks at 244, 182, 163, 143 and 98 K, marked with A_1, B_1, C_1, D_1 and E_1. The relative modulus ΔE decreases slowly and monotonically with increasing temperature close to 182 K, and does not show any anomalous change. Corresponding to the appearance of the B_1 peak at 182 K, ΔE conspicuously softens, and then it shows a weak minimum at 240 K, marked with an arrow in figure 3. The internal friction in figure 4 exhibits four distinct peaks at 249, 182, 151 and 98 K, marked with A_2, B_2, D_2 and E_2. Compared with the B_1 peak, the asymmetric B_2 peak is enhanced and broadened and has a shoulder around 173 K which is shown in the inset of figure 4. To guide the eyes, the B_2 peak can be divided into two sub-peaks located at 173 (marked with C_2) and 182 K, respectively, by a nonlinear fitting method [17]. The fitting result is plotted in figure 5. ΔE in figure 4 shows a weak minimum at 245 K, marked with an arrow. Compared with results of ρ and M, Q^{-1} seems to supply more detailed information.

In region 2, the temperature positions of both B_1 and B_2 peaks stay at 182 K on raising the measuring frequency from 1.80 to 4.97 kHz, which is characteristic of phase transition internal friction. Accompanying the appearance of the B_1 peak at 182 K, ΔE shows a prominent softening with increasing temperature. The large softening of ΔE may reflect the rapid increase of the volume of MnO_6 octahedra as suggested in [18] recently. For the electron–phonon coupling of $1.4 < \lambda < 1.65$, a strong coupling between the spin and lattice also occurs, i.e. the FM–PM transition is accompanied by a sharp increase of the volume of MnO_6 octahedra, and the transition is of the first order [18]. So it can be suggested that the peak B_1 may be related to the first order transition from FM to PM phase upon heating.

The A_1 peak at 244 K shifts to the A_2 peak at 249 K on raising the measuring frequency from 1.80 to 4.97 kHz, indicating a characteristic of thermally activated relaxation. Based
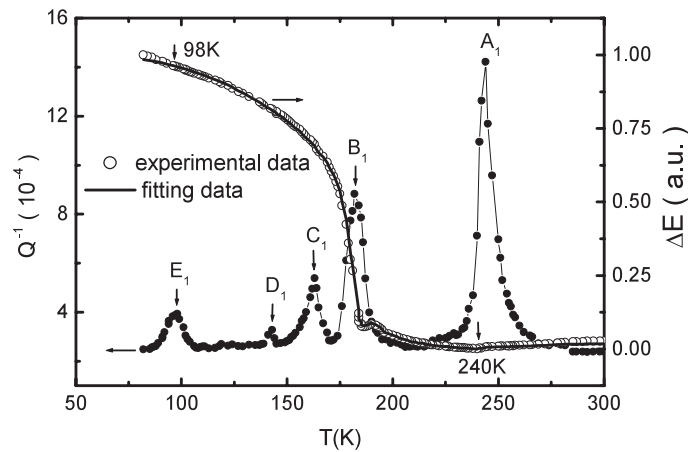
Figure 3. The temperature dependence of the internal friction Q^{-1} and relative Young modulus ΔE measured at the frequency of 1.80 kHz for $La_{0.8}Ca_{0.2}MnO_3$ at zero magnetic field; the solid curve is the fitting curve for ΔE according to the equation $\Delta E = \tanh[\Delta E/(T/T_D)]$.
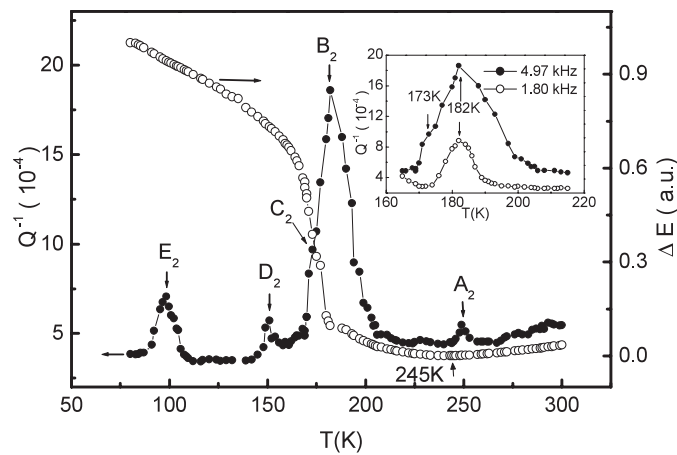

Figure 4. The main panel shows the temperature dependence of the internal friction Q^{-1} and relative Young modulus ΔE measured at the frequency of 4.97 kHz for $La_{0.8}Ca_{0.2}MnO_3$ at zero magnetic field. The inset shows the temperature dependence of the internal friction Q^{-1} around 182 K under the different measuring frequencies of 1.80 and 4.97 kHz.

on the resistivity in figure 1, the sample is still insulating at 244 K, indicating that the FM path does not percolate through the sample at this temperature, i.e. FM clusters are separated by the PM matrix. De Teresa *et al* suggest that a localized electron causes the local lattice distortion, macroscopically, the volume expansion, and, if an electron that becomes localized polarizes the spins of the neighbor ions due to FM exchange interaction, a magnetic polaron would form [9]. We think that if there exists local coupling between magnetic polarons, it is possible to form magnetic clusters (MCs) with nanometre scale size. Based on the result obtained by De Teresa *et al*, the local lattice distortion is a possible underlying driving force for the formation of MCs, and the coupling between spin and lattice may be responsible for both the anelastic relaxation effect and the internal friction peak at 244 K. For a thermally activated relaxation process, the relaxation time τ generally follows the Arrhenius relation [19]
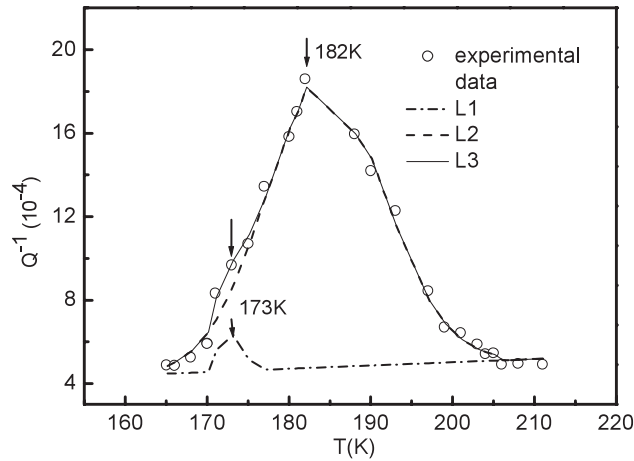
Figure 5. The temperature dependence of Q^{-1} at measuring frequency of 4.97 kHz around 182 K. The empty circles are experimental data points. The dashed (L2) and dashed–dotted (L1) lines are the fitting lines of the 182 and 173 K peaks, respectively. The internal friction values of L1 and L2 add up to those of L3 (solid curve).

$$\tau = \tau_0 \exp(E_a/k_B T), \tag{3}$$

where τ_0 is the pre-exponential factor (or the relaxation time at infinite temperature), E_a is the activation energy of the relaxation process and k_B is the Boltzmann constant. At the Q^{-1}-peak position, the condition $\omega\tau = 1$ is satisfied, where the angular frequency $\omega = 2\pi f$. By fitting, the activation energy E_a is deduced to be roughly 1.01 eV. The prefactor τ_0 is about 5.96×10^{-25} s, which is a completely unphysical value, and the cause of such small τ_0 may be a hint to an alternative mechanism which is unknown to us.

In region 1, the peak E_1 also exhibits the characteristic of phase transition internal friction. Peaks C_1 and D_1 are characteristic of thermally activated relaxation. The relaxation parameters E_a and τ_0 deduced from equation (3) are 0.23 eV, 6.38×10^{-13} s for the 143 K peak and 0.23 eV, 4.44×10^{-12} s for the 163 K peak. The internal friction peaks in region 1 are very similar to those observed in $La_{0.67}Ca_{0.33}MnO_3$ in the FM region [16]. In order to make a comparison conveniently, we also plot the temperature dependence of Q^{-1} and M of $La_{0.67}Ca_{0.33}MnO_3$ in the inset of figure 2.

As to the origin of internal friction peaks in region 1, it is reasonable to suggest that they are also closely related to the intrinsic inhomogeneity of the sample, as suggested in [20]. In fact, as Becker *et al* argued, the broad MIT implied the sample is inhomogeneous [21]. For our studied sample, figure 1 shows that there exists a 38 K difference between T_P and T_K. Generally, for a completely homogeneous sample, one would expect that the $\rho(T)$ curve would have a sharp transition and T_K should be very close to T_P when the sample undergoes a transition from metallic to insulating phase. So it is reasonable to suggest that an intrinsic inhomogeneity may exist in the $La_{0.8}Ca_{0.2}MnO_3$ sample that comprises insulating and conducting domains in the FM region which has been observed in manganites by ^{55}Mn NMR in previous studies [10, 11]. As to the peak E_1, we suggest that it also originates from the electronic phase separation, which means that the sample may be a single homogeneous FM metallic phase in the temperature range $T < 98$ K. As the temperature is increased to 98 K, an electrically insulating phase appears. Therefore, as $T > 98$ K, the sample comprises both metallic and insulating domains. The fraction of insulating domains increases and that of metallic domains decreases, which

results in the motion of the insulating and metallic domain boundary and contributes to the C_1 and D_1 peaks. The activated energies of domain boundary motion are 0.23 eV for both insulating and metallic domains, respectively. In the temperature range of 98–182 K, though the relative volumes of insulating and metallic domains are changed, the percolative path constituted by metallic domains does not become fully destroyed and the sample keeps up percolative conduction making the sample exhibit metallic behaviour. As temperature is increasing above $T_K \sim 186$ K, the fraction of metallic domains reduces rapidly resulting in a resistivity jump, and, at $T = T_P$, metallic domains are separated by insulating ones, resulting in the melting of the percolative path and giving rise to the occurrence of the MIT.

The electronic phase separation is close related to the local distortion disorder of the MnO_6 octahedron. Moreo *et al* [8] suggest that tendencies toward charge inhomogeneous states exist in real manganese oxides all around the FM phase in the temperature–density phase diagram. The charge inhomogeneous state is evidenced experimentally by the results of high-real-space-resolution atomic pair distribution functions obtained from the high-energy x-ray powder diffraction technique [22] in $La_{1-x}Ca_xMnO_3$ ($x = 0.12, 0.25$ and 0.33). The results of Billinge *et al* provided a distinct picture for the localization of charge carriers. In a homogeneous FM metallic phase, the sample exhibits a single Mn–O bond. However, with increasing temperature, long Mn^{3+}–O bonds begin to appear, which means the appearance of JT distortion of the MnO_6 octahedron. This distortion results in the localization of the e_g electron and gives rise to the appearance of the insulating phase. Similar results are observed in $La_{1-x}Ca_xMnO_3$ ($x = 0.12, 0.21$ and 0.25) [23]. It is reported that if the carriers are completely delocalized, the carrier charge density is evenly distributed among the Mn sites and there are no distinct Mn^{3+} and Mn^{4+} ions. An average distortion to the octahedron will exist but there will be well defined Mn–O bond lengths which are fully ordered.

The temperature dependence of ΔE can be well fitted by the equation

$$\Delta E = \tanh[\Delta E/(T/T_D)]. \tag{4}$$

The fitting result is also plotted in figure 3, and the fitting parameter T_D is 198 K. Accurately, the Young modulus E, microscopically, reflects the strain among the atoms. According to the Hooke law [19], strain e and stress σ are satisfied by the relation $\sigma_i = \sum_j C_{ij}e_j$, where C_{ij} is a 6×6 matrix. In an isotropic condition, $c_{11} = c_{12} + 2c_{44}$ is satisfied. In the condition of a tensile strain, E is equal to $\frac{c_{44}(3c_{12}+2c_{44})}{c_{12}+c_{44}}$. Therefore, E, C_{ij} and e are interrelated, and, moreover, the elastic constant C_{ij} microscopically reflects the information on electronic band structure, ferroelectric fluctuations or the JT effect [24]. In addition, the cooperative JT distortion [25] in the $TmVO_4$ system [26] can be described by

$$e(T)/e^0 = \tanh[(e(T)/e^0)/(T/T_D)], \tag{5}$$

derived from a mean-field approximation, where e^0 is the static strain at the absolute zero temperature. The reduced $e(T)/e^0$ has a similar equation to ΔE, so ΔE may also reflect the cooperative JT distortion in $La_{0.8}Ca_{0.2}MnO_3$ if we assume the e value at the lowest temperature, 80 K, to be e^0. Near the magnetic transition, the fitting data match the experimental ones, which indicates that the cooperative JT distortions develop accompanying the PM–FM transition. However, there exist some deviations below 98 K, which may result from the reduction of cooperative Jahn–Teller distortion due to the delocalized charge carriers in the homogeneous metallic FM region.

4. Conclusion

In summary, the behaviour of the FM manganite $La_{0.8}Ca_{0.2}MnO_3$ sample below the MIT has been investigated by internal friction Q^{-1} and Young's modulus E measurements. In addition

to the Q^{-1} peaks at temperatures 182 and 244 K in region 2, the other three Q^{-1} peaks located at 98, 143 and 163 K are also detected. We suggest that the 98 K peak originates from the electronic phase transition induced by the local distortion disorder of the MnO_6 octahedron, which gives rise to the coexistence of metallic and insulating domains in the temperature region of 98 K $< T < T_P$. The results reveal the nature of the intrinsic inhomogeneity of the sample in the FM phase. The other two peaks at 143 and 163 K are the dynamic characteristics of insulating and conduction domains and reflect the thermally activated relaxation motion of two kinds of domains. Our results indicate that the internal friction method seems to be a useful technique in studying the coupling between the spin, charge and lattice of CMR materials.

Acknowledgments

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