

## High-frequency magnetoimpedance of double perovskite $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ : Secondary transitions at high temperatures

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Radio frequency magnetoimpedance measurements reveal a pronounced anomaly at 260 K besides the main metal-insulator transition at 125 K in the double-perovskite material  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ . This feature is not seen clearly in static resistivity and magnetization measurements. We suggest that this anomaly represents short-range magnetic correlations enhanced at radio frequencies, with the easy axis along the  $c$  axis.

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The observation of colossal magnetoresistance (CMR) in perovskite manganites  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $A = \text{Sr}, \text{Ca}$ ) (113) has triggered further research into related systems.<sup>1-4</sup> The CMR in these materials is normally observed at temperatures close to the ferromagnetic-to-paramagnetic transition associated with a metal-insulator (MI) transition. Following the double-exchange mechanism of Zener,<sup>5</sup> based upon the strong on-site (Hund's rule) coupling between the charge carriers ( $e_g$ -like state) and the local spins ( $t_{2g}$ -like state), several models<sup>6-10</sup> have been proposed to account for these properties, but many of the observed features cannot be accounted by the double-exchange interaction alone. These well-studied 113 compounds can be considered as the  $n = \infty$  members of the Ruddlesden-Popper (RP) series  $(\text{La}_{1-x}\text{Sr}_x)_{n+1}\text{Mn}_n\text{O}_{3n+1}$  which can be described as intergrowths between  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  perovskite blocks and rock salt-type layers  $(\text{La}, \text{Sr})\text{O}$ .

In order to examine further the relation between CMR, magnetic, and MI transitions, attention has been focused on other materials with reduced dimension  $n$ .<sup>11-14</sup> In particular, for the  $n=2$  member of the RP series  $(\text{La}_{1-x}\text{Sr}_x)_{n+1}\text{Mn}_2\text{O}_7$  (327), the material is antiferromagnetic for  $x=0$ , while in the region  $0.2 \leq x \leq 0.4$  the material is ferromagnetic and exhibits a MI transition at  $T_c$ . The maximum  $T_c = 125$  K obtained in this series is for  $x=0.4$ . Moritomo *et al.*<sup>15</sup> have reported a high value of the CMR in  $x=0.4$  composition at temperatures near and far away from  $T_c$ .

Most of the experiments that probe the manganites are static in nature and have limited capabilities in elucidating the basic mechanisms involved. Recent dynamic measurements like electron paramagnetic resonance<sup>16</sup> (EPR) and ferromagnetic resonance<sup>17</sup> (FMR) have provided microscopic evidence for the formation of Jahn-Teller polarons and spin-wave resonance, respectively, in the manganites. In  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , Srikanth *et al.*<sup>18</sup> have very recently observed additional new features in the rf impedance measurements, which are not clearly visible in the dc resistivity and magnetization measurements. These results show that the dynamic rf measurements reveal new transitions, and in addition also give information on the collective response of spin

and charge dynamics. In this paper we describe the temperature and field dependence of the radio frequency dynamic response of the double perovskite  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ . We focus on a pronounced anomaly around 260 K observed in many samples and suggest that this anomaly represents magnetic correlations, perhaps two dimensional (2D) in nature, with a single energy and temperature scale.

Single crystals (5 cm long and 0.5 cm diameter) of  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  were grown from the melt by the floating-zone method using a mirror furnace.<sup>19</sup> Powder x-ray diffraction (XRD) analysis resulted in the lattice parameters  $a = 3.864 \pm 0.002$  Å and  $c = 20.130 \pm 0.006$  Å, in close agreement with those previously reported.<sup>15</sup> The polycrystalline material was synthesized by the conventional solid-state sintering technique. No extra phases were detected by XRD and the lattice parameters were found to be identical to those determined in the case of the single crystals. Three single crystals labeled SC1, SC2, and SC3, and a polycrystalline sample labeled PC were studied.

The rf measurements were carried out using an ultrastable tunnel diode oscillator. The sample is placed in a coil which forms the inductive part of the  $LC$  resonant circuit. In this technique, a change in the effective reactance  $X$  of the sample, caused by varying the temperature  $T$ , magnetic field  $H$ , or angle  $\theta$  (between crystallographic axis and  $H$ ), leads to a change in the inductance of the coil which in turn results in a shift of the resonant frequency of the oscillator. The quantity that is measured is the change in the resonant frequency,  $df(T) = [f(T) - f_0(T)] - [f(T=270) - f_0(T=270)]$ , where  $f_0(T)$  is the empty coil frequency. From the elementary consideration of ac impedance and Maxwell's equations for magnetic, conducting materials, it can be shown that  $df = -G(dX) \propto -d(\mu\rho)^{1/2}$ . Here,  $dX(T, H, \theta) = X(T, H, \theta) - X(T=270, H=0, \theta=0)$  is the change in reactance,  $G$  the geometric factor, and  $\rho(T, H)$  and  $\mu(T, H)$  are the resistivity and permeability of the magnetic material, respectively. The change in the reactance is calculated using the above relation.

The stability of the circuit is very high, typically, 1 Hz in 4 MHz and the operating frequency is in the range 2–4 MHz

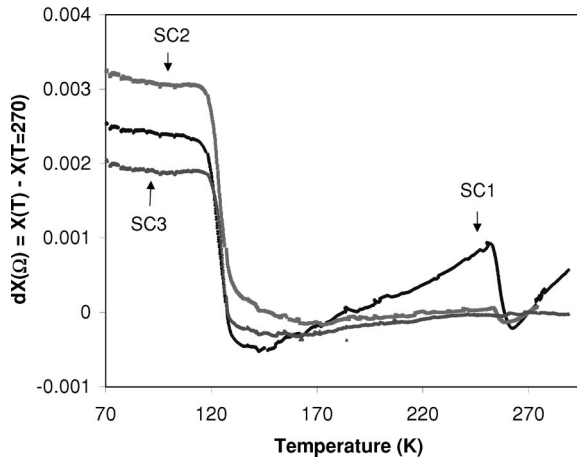


FIG. 1. Temperature dependence of radio frequency reactance for single crystals SC1, SC2, and SC3.

depending on the coil and sample used. The inductive coil with the sample is inserted into a helium flow cryostat and coupled through a rigid coaxial cable to enable a temperature variation between 4.2 and 300 K. In all the measurements the rf field is perpendicular to the  $c$  axis of the crystal. For field-dependent measurements, a dc magnetic field (up to 6 kOe) was applied by placing the sample coil-cryostat assembly between the pole pieces of an electromagnet.

The magnetization and CMR of the crystal have been described elsewhere.<sup>20</sup> Briefly, a sharp ferromagnetic to paramagnetic and (MI) transition is observed around 125 K, in the temperature dependence of the magnetization,  $M(T)$ , and resistivity,  $\rho(T)$ , measurements, respectively. However, a strong deviation from the Curie-Weiss law was noted at above  $T > 200$  K. Interestingly, in the case of sample SC1, while a very small change in slope is observed at around 260 K in the  $M(T)$ , no such anomaly is observed in the dc  $\rho(T)$  in both  $ab$ -plane ( $\rho_{ab}$ ) and  $\hat{c}$ -axis ( $\rho_c$ ) directions (inset, Fig. 2). From the field dependence of magnetization  $M(H)$  at 5 K it is found that the easy axis of magnetization lies in the  $ab$  plane which is in agreement with reported results.<sup>21,22</sup> The magnetic moment at  $H = 5$  T was found to be  $3.5\mu_B/\text{Mn}$  atom which is in close agreement with the theoretical value,  $3.6\mu_B/\text{Mn}$  atom, ensuring the almost 100% spin polarization of the conduction electrons due to a large Hund's-rule coupling energy.<sup>24</sup>

Figure 1 shows the shift in the radio frequency reactance  $dX$  as the temperature is varied between 300 and 70 K, for single crystals SC1, SC2, and SC3. As can be seen from the figure all the three single crystals show a sharp main transition at  $T_c = 125$  K. Results for the polycrystal sample PC (not shown) were similar but the transition at  $T_c$  was broadened. In the case of sample SC1, interestingly, a very strong jump, representative of a secondary transition, is observed at a temperature 260 K, which we call  $T^*$ . It is worth noting that the shift at this temperature is almost 35% of the shift at  $T_c$  and has similar characteristics as that of the transition at  $T_c = 125$  K. Such a transition is not seen in the static dc resistivity and is only observed as a very small change in slope in the magnetization measurements. Samples SC2, SC3, and PC also show similar but weaker transitions around the same temperature. While the first transition at 125 K is

the well-known MI transition [which is also observed in the dc  $M(T)$  and  $\rho(T)$  measurements], the origin of the transition at  $T^* = 260$  K is quite intriguing and worth studying.

In the magnetization measurements, very weak features are observed in the vicinity of  $T^*$ , but are nowhere as pronounced as in Fig. 1. In the literature similar weak features have been reported in double perovskite but have not been adequately addressed.<sup>15,22,23</sup> In the present ac measurements, the features are striking and unavoidable. In this paper we focus on this anomaly—a subsequent paper will discuss the details of the field and temperature dependence of the rf response over the entire temperature range. It is important to dwell on these unusual transitions as they may hold a key to an understanding of the basic mechanism involved in the CMR materials.

It was earlier demonstrated from a transmission electron microscopy (TEM) analysis that intergrowths could be present in these materials.<sup>25,22</sup> The intergrowths are missing or extra layers of SrO between  $\text{MnO}_6$  octahedra, which could form higher order ( $n > 2$ ) phases of RP series. The unit cell of 327 may be written as  $\text{SrO}(\text{La}_{1-x}\text{Sr}_x\text{MnO}_3)_2$ , where it is clear that  $\text{MnO}_6$  octahedra are separated from each other by an insulating SrO layer. If the second transition is thought to be due to the impurity 113 phase which forms due to the missing of SrO layers, then this phase is likely to be  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ . The corresponding transition temperature of this phase is well above 300 K.<sup>26</sup> Second, any phase transition in the  $\text{MnO}_3$  system is, generally, associated with a large CMR at the transition. From the  $\rho(T)$  it can be inferred that a large change in magnetoresistance is not observed at  $T^*$  even though as noted previously the overall magnetoresistance is substantial. Hence, the transition at  $T^*$  that we observe is not due to  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  but due to some other mechanism. The transition at  $T^*$  could not be due to any other impurity phases since experimental XRD (Ref. 20) and electron diffraction<sup>27</sup> studies show that the sample is free from impurity phases. Therefore, one can rule out the intergrowths or impurities playing any role in inducing this transition.

In Fig. 2 we present the effect of external field in the  $ab$  plane ( $H \parallel ab$ ) and along the  $\hat{c}$  axis ( $H \parallel c$ ). As can be seen from the figure, in the case of  $H \parallel ab$  the change in  $dX$  at the MI transition (at 125 K) decreases when compared to the same in the absence of field and, interestingly, the transition at  $T^*$  is almost smeared out. However, in the case of  $H \parallel c$  the change in  $dX$  at the MI transition increases and the transition at  $T^*$  disappears as in the case of  $H \parallel ab$ . Since the easy axis of the magnetization is in the  $ab$  plane, the decrease or increase in  $dX$ , in the case of  $H \parallel ab/H \parallel c$ , can be understood in terms of the decrease or increase in magnetization, respectively. If the  $T^*$  is due to an impurity phase (which ought to have an easy axis in certain direction), as is expected from the intergrowth mechanism, the  $dX$  at this temperature should have opposite responses for  $H \parallel ab$  and  $H \parallel c$  configurations, as in the case of the MI transition. The present response, unequivocally, suggests that the transition at  $T^*$  is not due to impurity phases or intergrowths. It instead suggests some kind of ordering with a weak exchange interaction which gets destroyed in the presence of moderate magnetic fields.

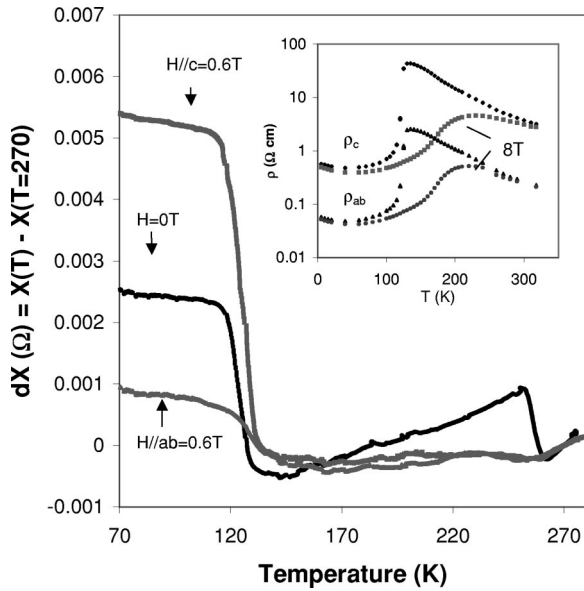


FIG. 2. Temperature dependence of rf reactance in the presence of a magnetic field,  $H=0.6$  T, for sample SC1.  $dX$  at  $T_c$  increases when the field is parallel to the  $c$  axis contrary to the behavior when the field is parallel to the  $ab$  plane. The inset shows the temperature dependence of resistivity in the  $ab$  plane and along the  $c$  axis, both in the presence and absence of field.

Recently, Moritomo *et al.*<sup>15</sup> have observed a transition around 275 K in  $x=0.4$  compositions. However, no case has been made to explain it. In the case of  $x=0.3$  compositions, Kimura *et al.*<sup>21</sup> observed a striking secondary MI transition in the  $ab$  plane ( $MI_{ab}$ ) resistivity, in addition to the usual MI transition around 100 K. They did not observe such a secondary MI transition in the  $c$ -axis resistivity measurements. The result was ascribed to the 2D ferromagnetic correlations within the  $MnO_2$  bilayers leading to a  $MI_{ab}$  transition at 275 K. The 3D spin ordering across the nonmagnetic insulating (La,Sr)O layers was suggested to be taking place at the  $T_c$ . However, in the present crystal but for the magnitude change in the resistivities  $\rho_{ab}$  and  $\rho_c$ , no further difference is observed (inset, Fig. 2). In both the cases in the temperature range  $T_c < T < T^*$  the sample shows insulating behavior.

The CMR, defined as  $-\frac{\rho(H) - \rho(0)}{\rho(0)}$ , is almost 100% for  $T_c < T < 150$  K and exceeds 10% in the entire temperature range. This CMR behavior is in sharp contrast with that of the  $La_{1-x}A_xMnO_3$  perovskite, where it is present only below and close to  $T_c$ .<sup>1-4</sup> The enhanced CMR in the present compound could be due to an anisotropic exchange interaction. The intralayer exchange interaction can be understood in terms of double exchange. Below  $T_c$  the interlayer coupling is established which contributes to the 3D magnetic ordering. The very large CMR observed in the vicinity of  $T_c$ , both below and above, is due to the alignment of the  $t_{2g}$  spins in the presence of an applied magnetic field which reduces the scattering of the carriers by the local spins. The fact that a large CMR is observed even above  $T_c$  indicates that some kind of spin correlation is maintained in this region. There could be many competing interactions and ordering above  $T_c$  such as antiferromagnetic superexchange, electron lattice (the Jahn-Teller effect), and charge ordering. From an inelastic neutron scattering study it was earlier in-

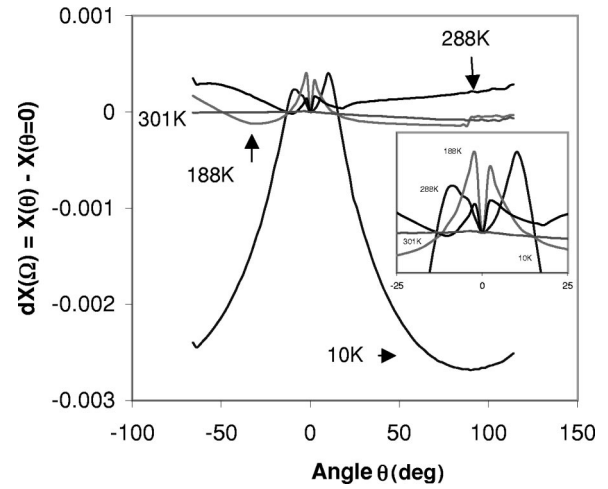


FIG. 3. Angular variation of rf reactance,  $dX$  vs  $\theta$  (angle between the dc field and  $c$  axis of the crystal), in the presence of a 0.3 T field at various temperatures for sample SC1. The variation at small  $\theta$  is shown in the inset for clarity. The minimum at  $0^\circ$  is associated with the secondary transition at  $T^*$  while the minimum at  $90^\circ$  is associated with ferromagnetic ordering below  $T_c$ .

ferred, in the case of  $x=0.4$  double perovskite, that the spins in the neighboring layers are strongly canted<sup>28</sup> and that there exists in-plane antiferromagnetic (AF) correlations above  $T_c$  which lead to insulating behavior.<sup>29</sup> In the present crystals also from the inelastic neutron scattering study<sup>30</sup> it has been observed that there is a coexistence of antiferromagnetism and ferromagnetism above  $T_c$ . Such a competition between ferromagnetic double exchange and antiferromagnetic superexchange has frequently been observed in the manganites which show a large negative CMR at temperatures above  $T_c$  because of the field suppression of the AF fluctuations.<sup>31</sup>

However, a careful analysis of the present results of  $x=0.4$  compositions indicates that the transition at  $T^*$  is not due to antiferromagnetic correlations but, probably, due to weak ferromagnetic correlations. The results show that the main transition at  $T_c$  and the secondary transition at  $T^*$  are similar in nature.

In Fig. 3 the change in reactance,  $dX$ , in the presence of a 0.3 T magnetic field, as a function of the angle between the field and  $\hat{c}$  axis of the crystal at various temperatures, is shown. The response at 10 K can be considered purely magnetic since the field has no effect on  $\rho$  at this temperature (inset, Fig. 2). It can be seen that the overall response shows a reduction in permeability with an increase in the angle from  $0^\circ$  to  $90^\circ$ . Since the easy axis of the 327 phase is in the  $ab$  plane, this reduction in  $\mu$  is expected. However, at low angles one can see an increase in permeability which we identify as the response due to the secondary phase. It is worth noting that the minima are separated by exactly  $90^\circ$ . Therefore, it is not improper to conclude that the easy axis of the secondary phase is along the  $\hat{c}$  axis. This result coupled with the  $dX(T)$  provides strong evidence that the transition at  $T^*$  is ferromagnetic in nature and is independent of the ferromagnetic transition at  $T_c$ . Above  $T_c$  ( $T=188, 280,$  and  $301$  K) it can be seen that a much reduced response (change in  $\mu$ ) persists. The reason for this small change is the exis-

tence of ferromagnetic fluctuations above  $T_c$  which is evidenced by the ferromagnetic hysteresis loop even at 295 K.<sup>20</sup> The aforementioned field-dependent anisotropy (Fig. 3) and temperature-dependent (Figs. 1 and 2) measurements clearly suggest two kinds of ferromagnetic correlations occurring intrinsically.

It is very interesting to note that the neutron diffraction study by Mitchell *et al.*<sup>32</sup> shows a clear change in slope  $d(a, b \text{ axis})/dT$  at 260 K in the  $a, b$ -axis vs temperature plot. However, they do not observe any change in  $d(c \text{ axis})/dT$  at 260 K. Together, these two points clearly indicate that the  $T^*$  is most probably associated with spin-lattice coupling and the associated ferromagnetic correlations lie in the  $ab$  plane. Local lattice or Jahn-Teller distortions of the perovskite unit cells could lead to spin-lattice coupling. The coupling of the double exchange to the lattice degrees of freedom in manganites is theoretically studied by Millis *et al.*<sup>10</sup> and Roder *et al.*<sup>33</sup> in terms of magnetoelastic polarons. The deviation from linearity in the temperature dependence of the lattice parameters of  $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.3}\text{MnO}_3$  (Ref. 34) and  $\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$  (Ref. 35) was, earlier, interpreted in terms of a transition from large to small polarons. In the present case, the suggested 2D nature of the secondary transition

indicates that it is probably due to the formation of small magnetoelastic polarons.

The present secondary transition is very important in understanding the microscopic picture of the manganites. Such intrinsic spin-lattice coupling can be sensitive to impurities in the crystal, which may be the reason for not observing  $T^*$  clearly in samples SC2 and SC3. It is worth mentioning that similar high-frequency studies on very-high-quality single crystals of perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_7$  high-temperature superconductors gave rise to many novel features<sup>36,37</sup> which are not observed in general. In conclusion we have presented the temperature and field dependence of a dynamic radio frequency permeability study of the double perovskite  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ . These results indicate a secondary transition at 260 K similar to the main MI transition at 125 K. This anomalous secondary transition could be due to ferromagnetic correlations which are independent of the ferromagnetic ordering at  $T_c$ , which affect the dynamic permeability but are weakly coupled to charge transport.

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