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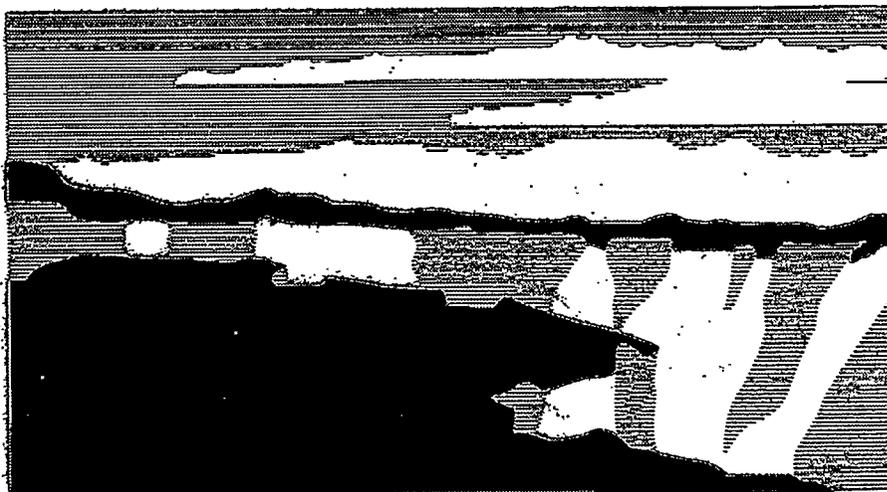
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## Transport and Magnetism Correlations in Thin-Film Ferromagnetic Oxides

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In order to determine the  $T_C$ -dependence of the colossal magnetoresistance (MR) exhibited by the ferromagnetic  $La_{0.7}M_{0.3}MnO_{3+\delta}$  ( $M = Ba, Ca, Sr$ ) system, we examine the magnetic-field and temperature dependent resistivity and magnetization of a series of thin films that were grown via pulsed-laser deposition. The films had magnetic ordering temperatures ( $T_C$ ) ranging from 150 to 350 K; all samples displayed a large negative MR that is largest near  $T_C$ . The magnitude of a given sample's MR at  $T_C$  inversely correlates with  $T_C$ ; samples with a low  $T_C$  display significantly larger MR values than do samples with large  $T_C$ 's. The quantity  $\rho(T_C)/\rho(4\text{ K})$ , the amount by which the resistivity is reduced by full ferromagnetic order, is an activated function of  $T_C$  with an activation energy  $E_a = 0.1\text{ eV}$ . These results indicate that the magnitude of the CMR effect in a given specimen is controlled not by  $\rho(T_C)$ , but by  $T_C$  via the ratio  $\rho(T_C)/\rho(4\text{ K})$ . Phenomenological scaling relationships are also reported that link  $\rho(H,T)$  to both  $H$  and  $M(H,T)$ .

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The recent observations<sup>1,2,3</sup> of a colossal negative magnetoresistance (MR) near  $T_C$  in the ferromagnetic (FM) doped lanthanum manganites ( $\text{La}_{1-x}\text{M}_x\text{MnO}_{3+\delta}$ ,  $\text{M} = \text{Ba}, \text{Ca}, \text{Sr}$ ) has sparked renewed interest in this system. The divalent substitution for  $\text{La}^{3+}$  leads to a mixed  $\text{Mn}^{3+/4+}$  valance, a ferromagnetic ground state driven by double-exchange,<sup>4</sup> a metal-insulator transition at  $T_{\text{MI}} = T_C$ , and the colossal magnetoresistance (CMR) effect. The unusual temperature and magnetic (H) field dependent resistivity exhibited by these compounds reflects a novel interplay between magnetism and electronic transport that does not occur in conventional metals, ferromagnets, or semiconductors. Recent publications have focused on the magnitude of the MR effect,<sup>3</sup> the interplay between magnetic order and electronic transport,<sup>5,6,7</sup> and the effects of oxygen stoichiometry<sup>8</sup> on the transport and magnetic properties.

In order to determine the dependence of the CMR effect on  $T_C$  we examine the temperature and H-field dependent resistivity  $\rho(\text{H},\text{T})$  of a series of  $\text{La}_{0.7}\text{M}_{0.3}\text{MnO}_{3+\delta}$  thin-films ( $\text{M} = \text{Ba}, \text{Ca}, \text{and Sr}$ ) with  $T_C$ 's ranging from 150 K to 350 K. Both the zero-field resistivity and the magnetoresistance are strongly dependent upon a given film's ordering temperature; low- $T_C$  films exhibit a substantial negative MR while films with  $T_C$ 's above 300 K exhibit a more modest MR ratio. We also find that a direct correlation exists between  $\rho(\text{H},\text{T})$  and  $M(\text{H},\text{T})$  near and below  $T_C$ . In addition, the MR at  $T_C$  follows a simple phenomenological expression that contains a single scaling parameter which is a monotonic function of  $T_C$ . The form of this scaling expression as well as the expression that links  $\rho(\text{H},\text{T})$  and  $M(\text{H},\text{T})$  provide important clues as to the nature of the underlying mechanisms responsible for the CMR effect.

Transport and magnetism measurements were performed on a series of six  $\text{La}_{0.7}\text{M}_{0.3}\text{MnO}_{3+\delta}$  thin films grown via pulsed-laser deposition (PLD). The highly oriented, 1000 Å-

thick films were deposited on (100)  $\text{LaAlO}_3$  substrates in a 200 mTorr oxygen atmosphere. The films were post-annealed in flowing oxygen at 950 °C for ten hours. Sample  $T_C$  was controlled both by varying the dopant element  $M$ ,<sup>9</sup> and by varying the substrate temperature  $T_S$  used during the deposition process. Growth parameters for each film, along with their respective magnetic ordering temperatures, are presented in Table 1. The Ca-doped films (films 1-4) have  $T_C$ 's ranging from 150 K to 290 K, while the Ba and Sr-doped films (films 5 and 6) have  $T_C$ 's that are above room temperature. Details of the underlying sample-to-sample differences (stoichiometry, microstructure, etc.) that are responsible for the variation in  $T_C$  in the Ca-doped samples will be considered in a future publication;<sup>10</sup> the variation is most likely due to an oxygen deficiency ( $\delta < 0$ ) that rises with increasing  $T_S$ .<sup>8</sup> The post-annealed films were patterned with conventional photolithography and ion milling into a four-terminal configuration suitable for resistivity measurements. Electrical contacts were made with silver conductive paint. Four-probe  $\rho$  measurements were made with dc currents ranging from 1 nA to 10  $\mu\text{A}$ . The magnetoresistance is defined here as  $\Delta\rho/\rho_0 = (\rho(H) - \rho_0)/\rho_0$ , with  $\rho_0 = \rho(H=0)$ . Magnetization ( $M$ ) measurements were performed with a Quantum Design SQUID magnetometer.

The zero-field resistivity of the films with  $T_C < 300$  K are depicted in Fig. 1a. Sample 1 ( $T_C = 152$  K) exhibits a sharp drop in  $\rho$  below  $T_C$  [ $\rho(4\text{K})/\rho(T_C) = 5 \times 10^{-4}$ ] and activated behavior (activation energy  $E_a \approx 0.1$  eV) above  $T_C$ . Samples 2 and 3 also exhibit activated behavior above  $T_C$  with similar  $E_a$  values. For the other samples  $\rho(T_C)$  progressively decreases with increasing  $T_C$ . Well below  $T_C$ ,  $\rho$  saturates to a value near 100  $\mu\Omega\text{-cm}$  for all samples. When normalized by their respective low-T resistivities,  $\rho(T > T_C)$  roughly fall on a common curve for all samples.

The T-dependent magnetoresistance MR(T) in 50 kOe is shown in Fig. 1b. Sample 1 displays a wide, flat-topped peak centered at  $T_C$  with a maximum MR of  $\Delta\rho/\rho_0 = -0.996$ . With increasing  $T_C$  the MR data indicate the following trends: (a) the width of the MR peak decreases, (b) the MR peak temperature  $T_{\max}$  shifts somewhat below  $T_C$ , (c) the magnitude of the MR peak decreases, and (d)  $\Delta\rho/\rho_0$  is very small at  $T \ll T_C$  for all six films. MR(T) data measured in  $H < 50$  kOe indicate that  $T_{\max}$  approaches  $T_C$  as H is increased. The H-dependent magnetoresistance MR(H) for samples 1-6 at their respective ordering temperatures are shown in Fig. 2a in fields to 100 kOe. Sample 1's MR saturates at a value near  $\Delta\rho/\rho_0 = -1$  in 25 kOe; sample 2's MR also saturates, but in a larger H-field and at a smaller value of  $\Delta\rho/\rho_0$ . The magnetoresistance of samples 3-6 do not saturate even in the largest fields applied. Extrapolations of the MR data to  $H > 100$  kOe for these higher- $T_C$  films suggests that the saturation values of  $\Delta\rho/\rho_0$  decreases with increasing  $T_C$ .

The key finding from the MR(T,H) data presented in Figs. 1 and 2 is that the size of the CMR effect decreases with increasing film  $T_C$ . This result is summarized in Fig. 2b where  $\Delta\rho/\rho_0(50 \text{ kOe})$  at  $T_C$  is plotted against sample  $T_C$  for films 1-6. The 50 kOe field essentially saturates the MR of sample 1 ( $T_C = 152 \text{ K}$ ), reduces  $\rho$  by 50% for the film with a  $T_C$  near room temperature, and only reduces  $\rho$  by roughly 20% for the high- $T_C$  Sr-doped film (film 6). This CMR  $T_C$  dependence is simply a reflection of the fact that the order-induced drop in  $\rho$  that occurs below  $T_C$  is far larger in low- $T_C$  samples than in high- $T_C$  samples. This is made clear in Fig. 3, where  $\rho(T_C)$  in both zero field and 50 kOe is plotted versus  $1000/T_C$  for the six films; the resistivity is normalized by the low-temperature (4 K) saturation resistivity. The quantity  $\rho(T_C)/\rho(4 \text{ K})$  is a measure of the reduction in  $\rho$  brought on by complete FM order. In zero field

$\rho(T_C)/\rho(4\text{ K})$  is thermally activated with an activation energy  $E_a = 0.1\text{ eV}$ . This is the same activation energy evident in  $\rho(T > T_C)$  in films 1-3. The normalized resistivity in 50 kOe is essentially  $T_C$ -independent. The zero-field and 50 kOe results in Fig. 3 lead directly to the fit  $\Delta\rho/\rho_0(T_C) = \alpha \exp(-E_a/T_C) - 1$  that is displayed in Fig. 2b ( $\alpha = 20$ ). The data in Figs. 2b and 3 indicate that the key quantity that controls the MR in a given film is the normalized resistivity  $\rho(T_C)/\rho(4\text{ K})$  (which is set by  $T_C$ ), and not just  $\rho(T_C)$ . Hence, attempts to increase  $\rho(T_C)$  by growth non-optimization should also increase  $\rho(4\text{ K})$ , and would presumably have little effect on the magnitude of the CMR effect.

To determine how the enhancement in  $M$  and the huge drop in resistivity that occur below  $T_C$  are linked, measurements of  $\rho(H,T)$  and  $M(H,T)$  were made on sample 3 ( $T_C = 255\text{ K}$ ). The results are presented in Fig. 4a, where  $\rho(H,T)$  is plotted against  $M(H,T)$  rather than as a function of  $H$  or  $T$ . The data were measured at nine temperatures from 272 K to 10 K in fields to 50 kOe. The data exhibit a correlation encompassing a two order-of-magnitude variation in  $\rho$  that can be parameterized as  $\rho(H,T) \propto \exp\{-M(H,T)/M_0\}$ , with  $4\pi M_0 = 2.0\text{ kG}$ . The data follow this phenomenological expression both close to and below  $T_C$ ; the expression does not describe the data above 280 K where FM fluctuations are no longer present. The data in Fig. 4a clearly indicate that the magnetization and resistivity are inextricably linked in the FM state. A similar relationship exists for the  $MR(H)$  data plotted in Fig. 2a. The field-dependent data at  $T_C$  for all six films can be scaled via the expression  $\rho(H)/\rho_0(T_C) \propto \exp(-H/H_0)$ , where the scaling parameter  $H_0$  is  $T_C$ -dependent. The scaled data appear in Fig. 4b, with  $H_0(T_C)$  plotted in the inset. With the exception of sample 1 in fields sufficient to saturate that film's magnetoresistance, the data are qualitatively well-described by this phenomenological expression. The scaling parameter  $H_0$  is a

simple, monotonically increasing function of  $T_C$ . The relationship that links  $\rho$  and  $H$  follows directly from that between  $\rho$  and  $M$  because the magnetization varies quasi-linearly in  $H$  for fields much less than the saturation field at  $T_C$ .

The phenomenological relationships between  $\rho$ ,  $M$ , and  $H$  may provide insight into the form of the transport mechanism in the CMR films. In the double exchange (DE) model, which is thought to explain the magnetism in the CMR compounds,<sup>4</sup> the bandwidth  $W$  is proportional to the magnetization. Polaron hopping transport leads to a resistivity of the form  $\rho \propto \exp(-W)$ .<sup>11</sup> With  $W \propto M$ , polaron hopping and double exchange combine to give  $\rho \propto \exp(-M)$ , precisely that which is observed in Fig. 4a. A somewhat surprising feature of the data is the fact that this exponential relationship persists down to temperatures well below  $T_C$  where it is reasonable to expect, given the drastic drop in  $\rho$ , that the polarons will be delocalized and transport would proceed via a conventional metallic process. The data in Fig. 4a may indicate that the quasiparticles evolve into large polarons at temperatures well below  $T_C$ . Additional theoretical and experimental work is needed to clarify this point.

In conclusion, field-dependent resistivity measurements on a series of six PLD-grown CMR films indicate that the magnitude of the CMR effect is determined by a given film's magnetic ordering temperature. Films with a low  $T_C$  exhibit both a large drop in the resistivity in the FM state and a large, negative magnetoresistance, while both effects are significantly smaller in films with a high ordering temperature.

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Tables

sample number	M	x	T <sub>s</sub> (°C)	T <sub>c</sub> (K)
1	Ca	0.3	900	152
2	Ca	0.3	750	224
3	Ca	0.3	600	255
4	Ca	0.3	500	292
5	Ba	0.3	600	325
6	Sr	0.3	600	350

Table 1. Stoichiometry, substrate temperature T<sub>s</sub> , and magnetic ordering temperature T<sub>c</sub> for the six La<sub>1-x</sub>M<sub>x</sub>MnO<sub>3+δ</sub> thin-film specimens examined in this work. All films were post-annealed.

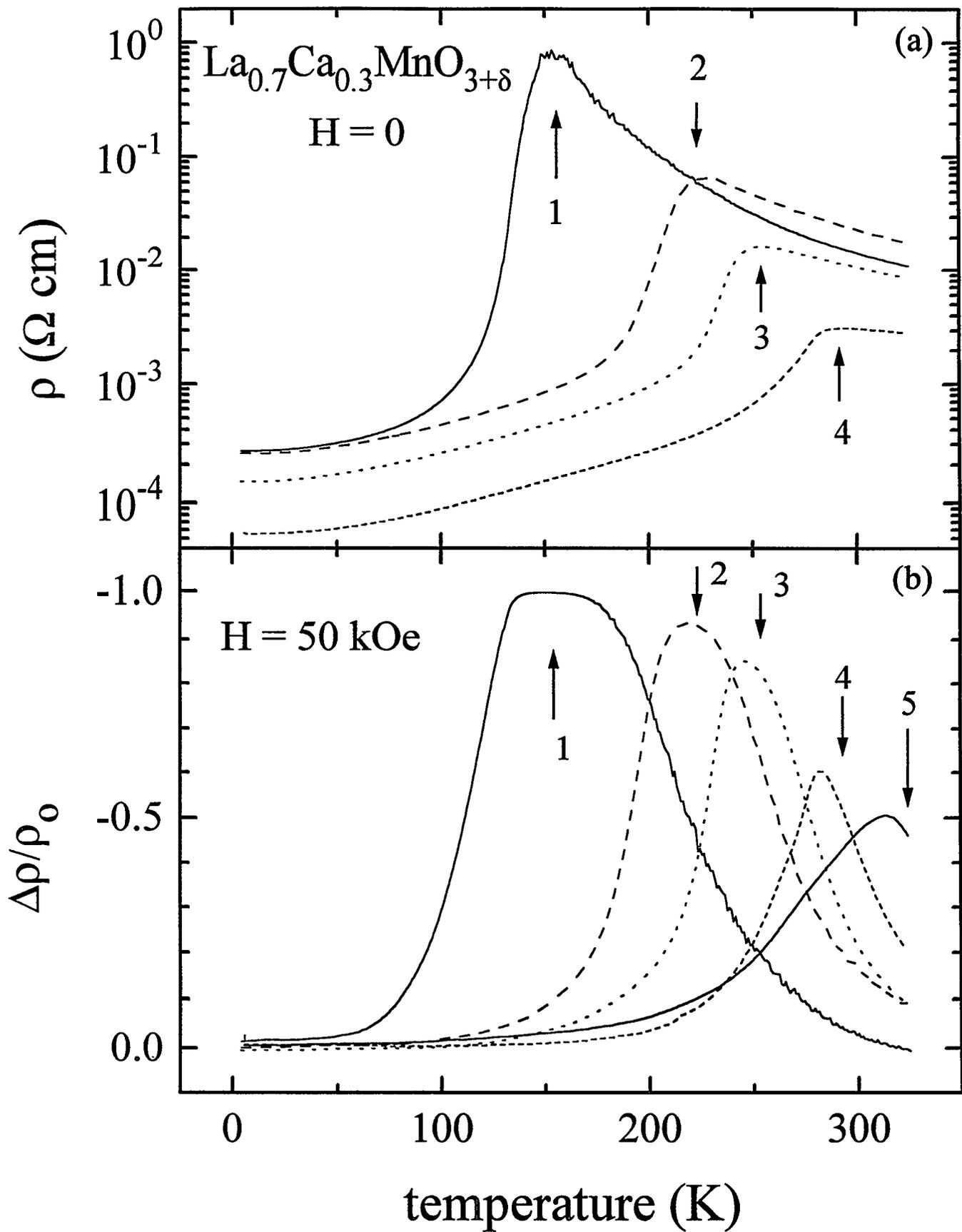
## Figure Captions

Figure 1: (a) Resistivity vs. temperature, and (b) 50 kOe magnetoresistance vs. temperature. The arrows indicate  $T_C$  for each sample while the integers indicate the sample number that corresponds to each data set.

Figure 2: (a) Magnetoresistance vs. applied magnetic field measured at  $T_C$  for six samples ( $T_C$  for each curve is indicated on the right). (b) 50 kOe Magnetoresistance measured at  $T_C$  for samples 1-6 plotted against sample  $T_C$ ; the solid line is a fit to the data (see text).

Figure 3: Normalized resistivity plotted against  $1000/T_C$  for samples 1-6 at their respective ordering temperatures in both zero field and 50 kOe.

Figure. 4: (a)  $\rho(H,T)$  vs.  $M(H,T)$  for sample 3. At each  $T$ , points are included at  $H = 10, 20, 30, 40,$  and  $50$  kOe. The solid line is a least-squares fit to the data. (b) Normalized magnetoresistance at  $T_C$  plotted vs.  $H/H_0$  for samples 1-6; the scaling parameter  $H_0$  is plotted against sample  $T_C$  in the inset.



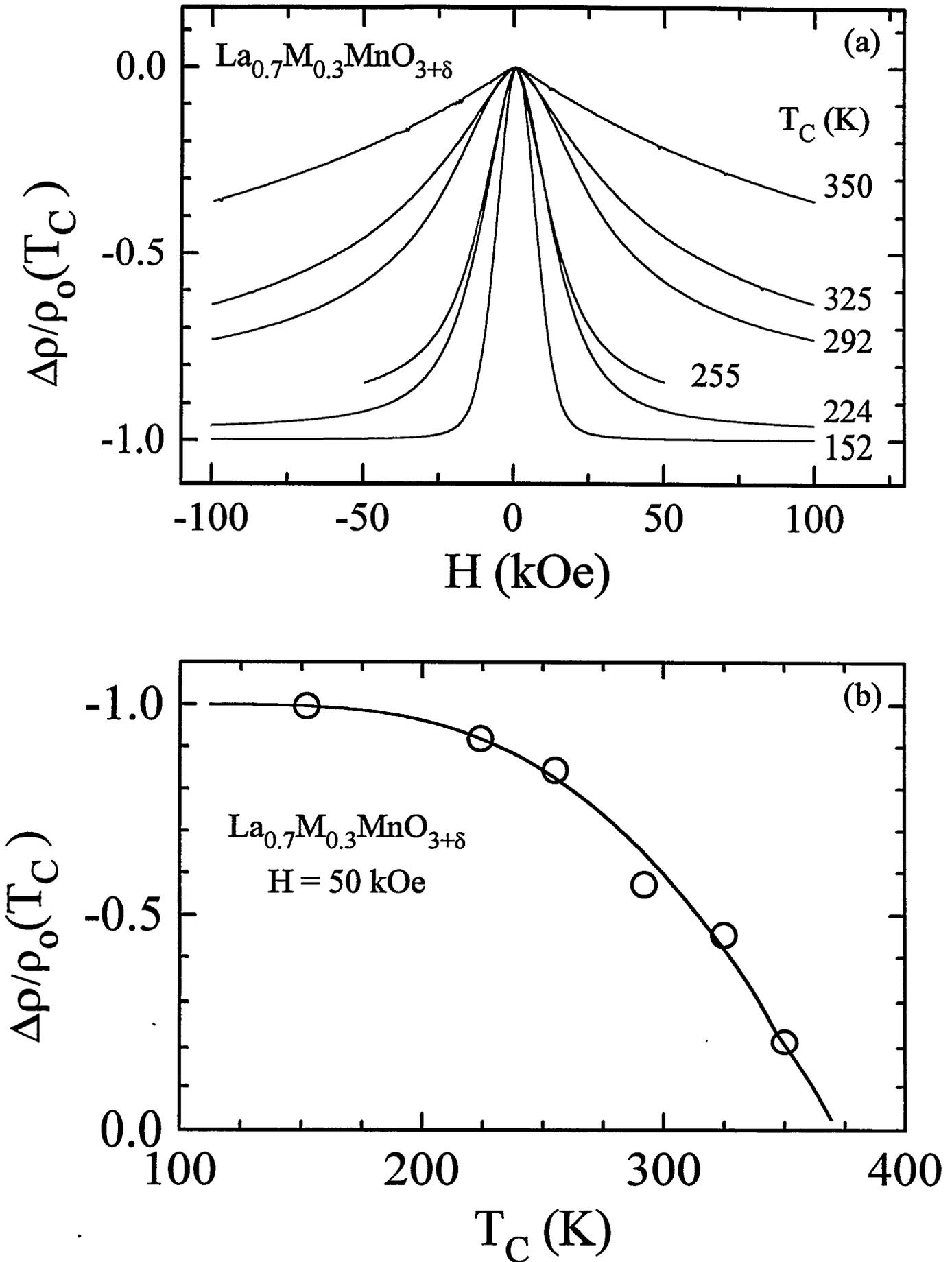


Figure 2 Hundley, et al. AC-0

