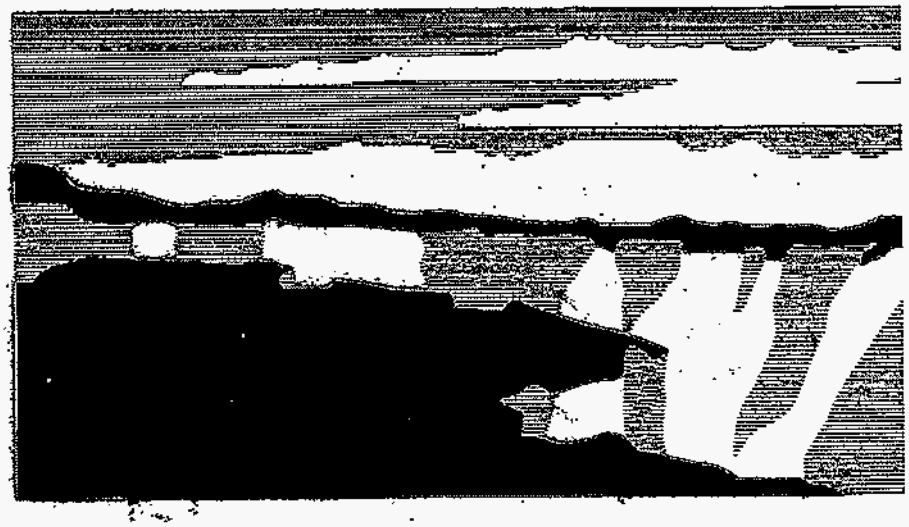
CONF-951101--4

LA-UR-95- 3027

Title: Transport and Magnetism Correlations in Thin-Film Ferromagnetic Oxides

Author(s):
M.F. Hundley
J.J. Neumeier
R.H. Heffner
Q.X. Jia
X.D. Wu
J.D. Thompson

Submitted to:
40th Magnetism and Magnetic Materials Conference
November 1995
Philadelphia, PA
Paper to be published in Journal of Applied Physics



Los Alamos
NATIONAL LABORATORY

Form No. 836 R5
ST 2629 10/91

manuscript AC-01

Transport and Magnetism Correlations in Thin-Film Ferromagnetic Oxides

M.F. Hundley, J.J. Neumeier, R.H. Heffner, Q.X. Jia, X.D. Wu, and J.D. Thompson

Materials Science and Technology Division

Los Alamos National Laboratory, Los Alamos, NM 87545 USA

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 $\rho(T_C)/\rho(4\ K)$, the amount by which the resistivity is reduced by full ferromagnetic order, is an activated function of T_C with an activation energy $E_a = 0.1$ 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 $\rho(T_C)/\rho(4\ K)$. Phenomenological scaling relationships are also reported that link $\rho(H,T)$ to both H and M(H,T).

PACS # : 75.50.Dd, 73.50.Jt, 71.38.+I, 71.30.+h

Submitted to the 40th MMM conference (1995)

The recent observations[1,2,3] of a colossal negative magnetoresistance (MR) near T_C in the ferromagnetic (FM) doped lanthanum manganites ($La_{1-x}M_xMnO_{3+\delta}$, M = Ba, Ca, Sr) has sparked renewed interest in this system. The divalent substitution for La^{3+} leads to a mixed $Mn^{3+/4+}$ valance, a ferromagnetic ground state driven by double-exchange,[4] a metal-insulator transition at $T_{MI} = T_C$, 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,[3] the interplay between magnetic order and electronic transport,[5,6,7] and the effects of oxygen stoichiometry[8] 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 $\rho(H,T)$ of a series of $La_{0.7}M_{0.3}MnO_{3+\delta}$ thin-films (M = Ba, Ca, 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 $\rho(H,T)$ and $M(H,T)$ 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 $\rho(H,T)$ and $M(H,T)$ 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 $La_{0.7}M_{0.3}MnO_{3+\delta}$ thin films grown via pulsed-laser deposition (PLD). The highly oriented, 1000 Å-

thick films were deposited on (100) $LaAlO_3$ 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,[9] 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;[10] the variation is most likely due to an oxygen deficiency ($\delta<0$) that rises with increasing T_S.[8] 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 ρ measurements were made with dc currents ranging from 1 nA to 10 μA. The magnetoresistance is defined here as $\Delta\rho/\rho_o = (\rho(H)-\rho_o)/\rho_o$, with $\rho_o = \rho(H=0)$. 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 ρ below T_C [$\rho(4K)/\rho(T_C) = 5x10^{-4}$] 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, ρ saturates to a value near 100 μΩ-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 $\Delta\rho/\rho_o$ = -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) $\Delta\rho/\rho_o$ 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 $\Delta\rho/\rho_o$ = -1 in 25 kOe; sample 2's MR also saturates, but in a larger H-field and at a smaller value of $\Delta\rho/\rho_o$. 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 $\Delta\rho/\rho_o$ 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 $\Delta\rho/\rho_o$(50 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 K), reduces ρ by 50% for the film with a T_C near room temperature, and only reduces ρ 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 ρ 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 $\rho(T_C)/\rho(4\ K)$ is a measure of the reduction in ρ brought on by complete FM order. In zero field

$\rho(T_C)/\rho(4\ K)$ is thermally activated with an activation energy E_a = 0.1 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 $\Delta\rho/\rho_o(T_C) = \alpha \exp(-E_a/T_C) - 1$ 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 $\rho(T_C)/\rho(4\ K)$ (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 $\rho(4\ K)$, and would presumably have little affect 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 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 is ρ that can be parameterized as $\rho(H,T) \propto \exp\{-M(H,T)/M_o\}$, with $4\pi M_o$ = 2.0 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 $\rho(H)/\rho_o(T_C) \propto \exp(-H/H_o)$, where the scaling parameter H_o is T_C-dependent. The scaled data appear in Fig. 4b, with $H_o(T_C)$ 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 Ho is a

simple, monotonically increasing function of T_C. The relationship that links ρ and H follows directly from that between ρ 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 ρ, 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,[4] the bandwidth W is proportional to the magnetization. Polaron hopping transport leads to a resistivity of the form $\rho \propto \exp(-W)$.[11] 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 ρ, 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.

This research was performed under the auspices of the U.S. Department of Energy.

References

1. K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993).
2. R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
3. S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen, Science **264**, 413 (1994); S. Jin, M. McCormack, T.H. Tiefel, and R. Ramesh, J. Appl. Phys. **76**, 6929 (1994).
4. C. Zener, Phys. Rev. **82**, 403 (1951); P.W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955); P.G. deGennes, Phys. Rev. **118**, 141 (1960).
5. M.F. Hundley, M. Hawley, R. Heffner, Q.X. Jia, J.J. Neumeier, J. Tesmer, J.D. Thompson, and X.D. Wu, Appl. Phys. Lett. **67**, 860 (1995).
6. J.Z. Sun, S.S.P. Parkin, L. Krusin-Elbaum, and Gang Xiao (unpublished).
7. M. Rubinstein, J.M Byers, R. Treece, P. Dorsey, J.S. Horwitz, and D.B. Chrisey (unpublished).
8. H.L Ju, J. Gopalakrishnan, J.L. Peng, Qi Li, G.C. Xiong, T. Venkatesan, and R.L. Greene, PRB **51**, 6143 (1995).
9. G.H. Jonker and J.H. van Santen, Physica **16**, 337 (1950).
10. R.H. Heffner, C. Adams, M. Hawley, M.F. Hundley, Q.X. Jia, J.J. Neumeier, J. Tesmer, J.D. Thompson, and X.D. Wu (unpublished).
11. I.G. Austin and M.F. Mott, Adv. Phys. **18**, 41 (1969).

Tables

sample number	M	x	T_S (°C)	T_C (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_S , and magnetic ordering temperature T_C for the six $La_{1-x}M_xMnO_{3+\delta}$ thin-film specimens examined in this work. All films were post-annealed.

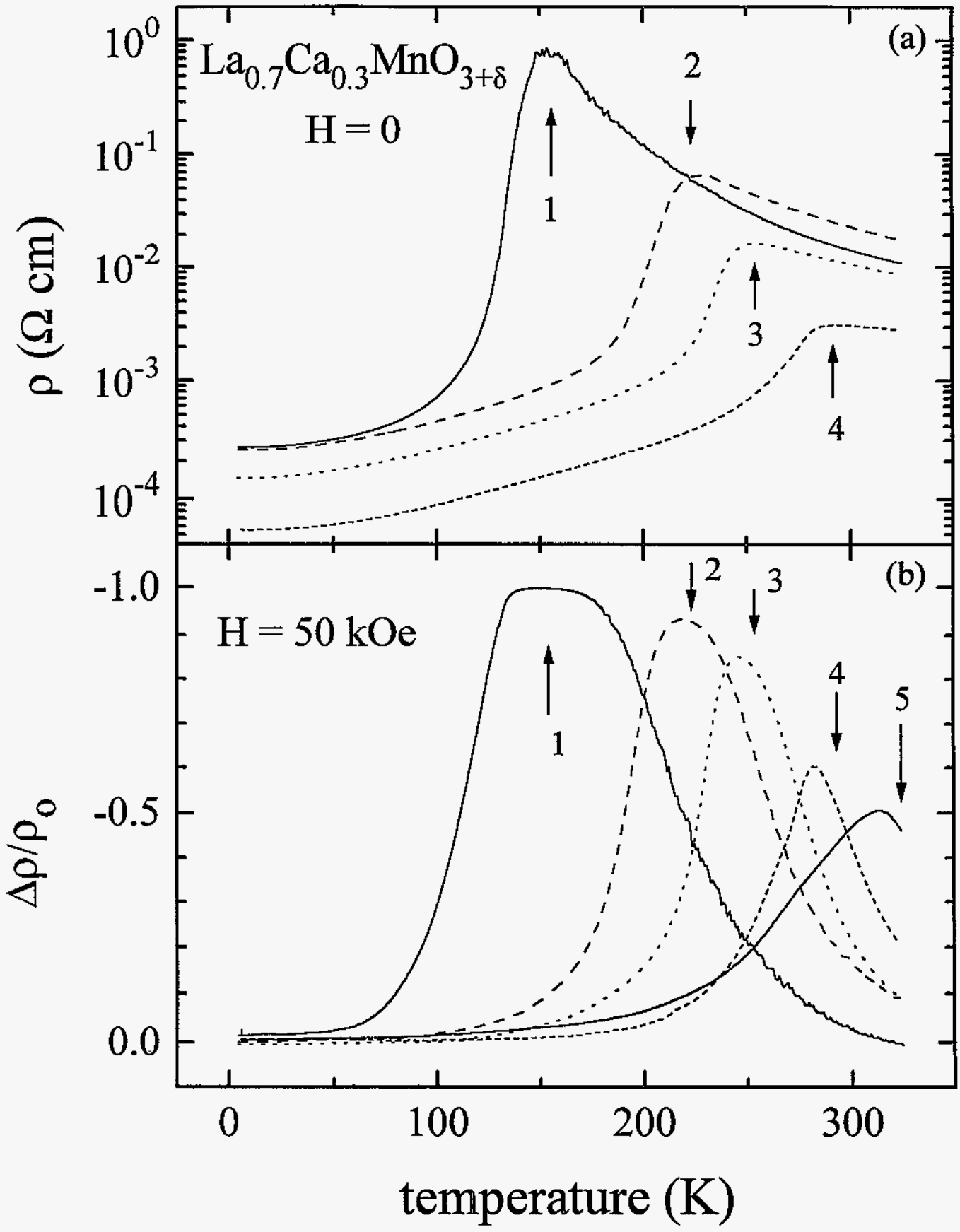
Figure Captions

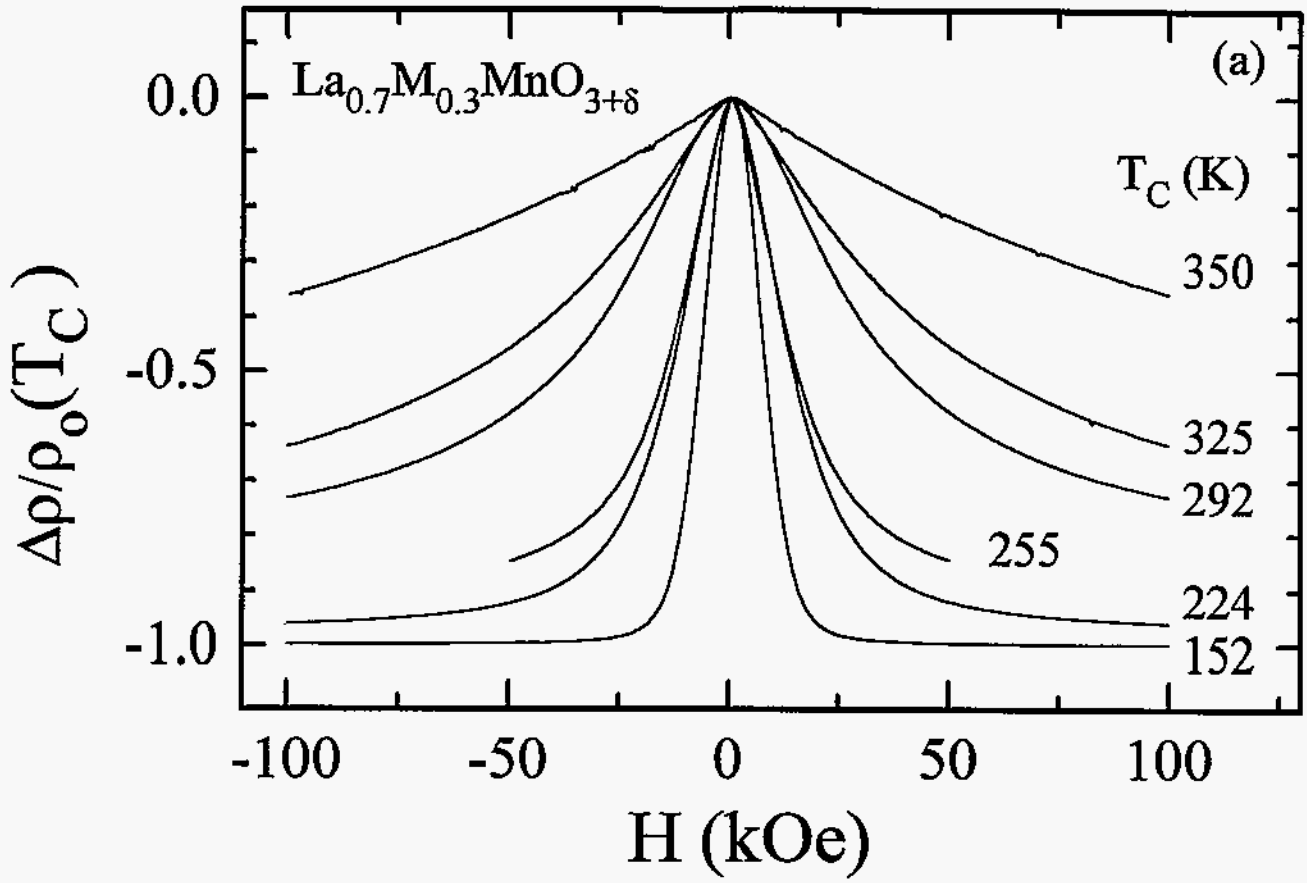
Figure 1: (a) Resistivity vs. temperature, and (b) 50 kOe magnetoresistance vs. temperature. The arrows indicate T_C for each sample while the integers indicate the sample number that corresponds to each data set.

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_o for samples 1-6; the scaling parameter H_o is plotted against sample T_C in the inset.


La0.7Ca0.3MnO3+δ
H = 0
(a)
1
2
3
4
ρ (Ω cm)
10^0
10^-1
10^-2
10^-3
10^-4
H = 50 kOe
(b)
1
2
3
4
5
Δρ/ρo
-1.0
-0.5
0.0
0
100
200
300
temperature (K)



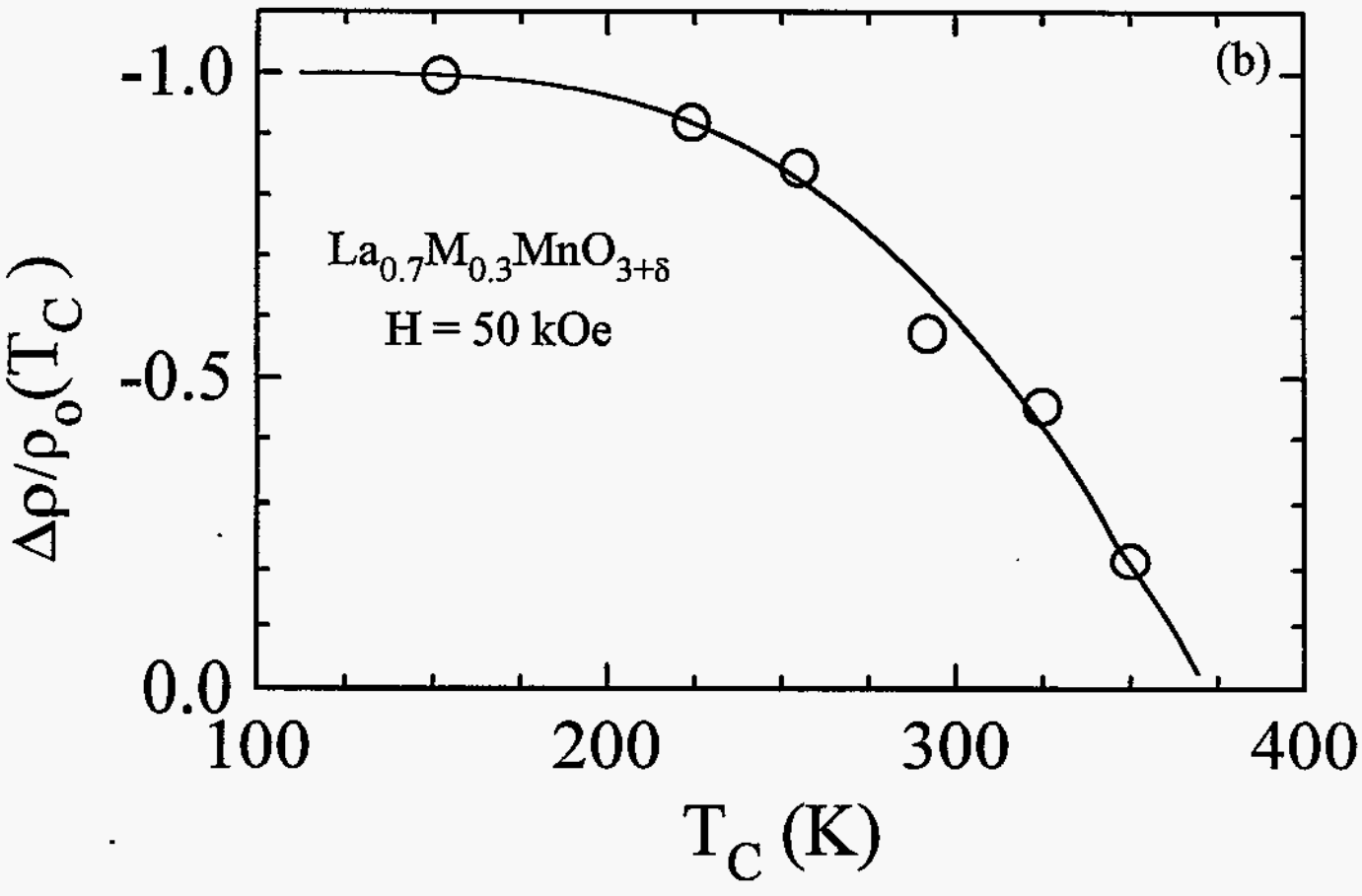


Figure 2 Hundley, et al. AC-0

MFH MST-10/LANL 8/15/95
mr895c.org

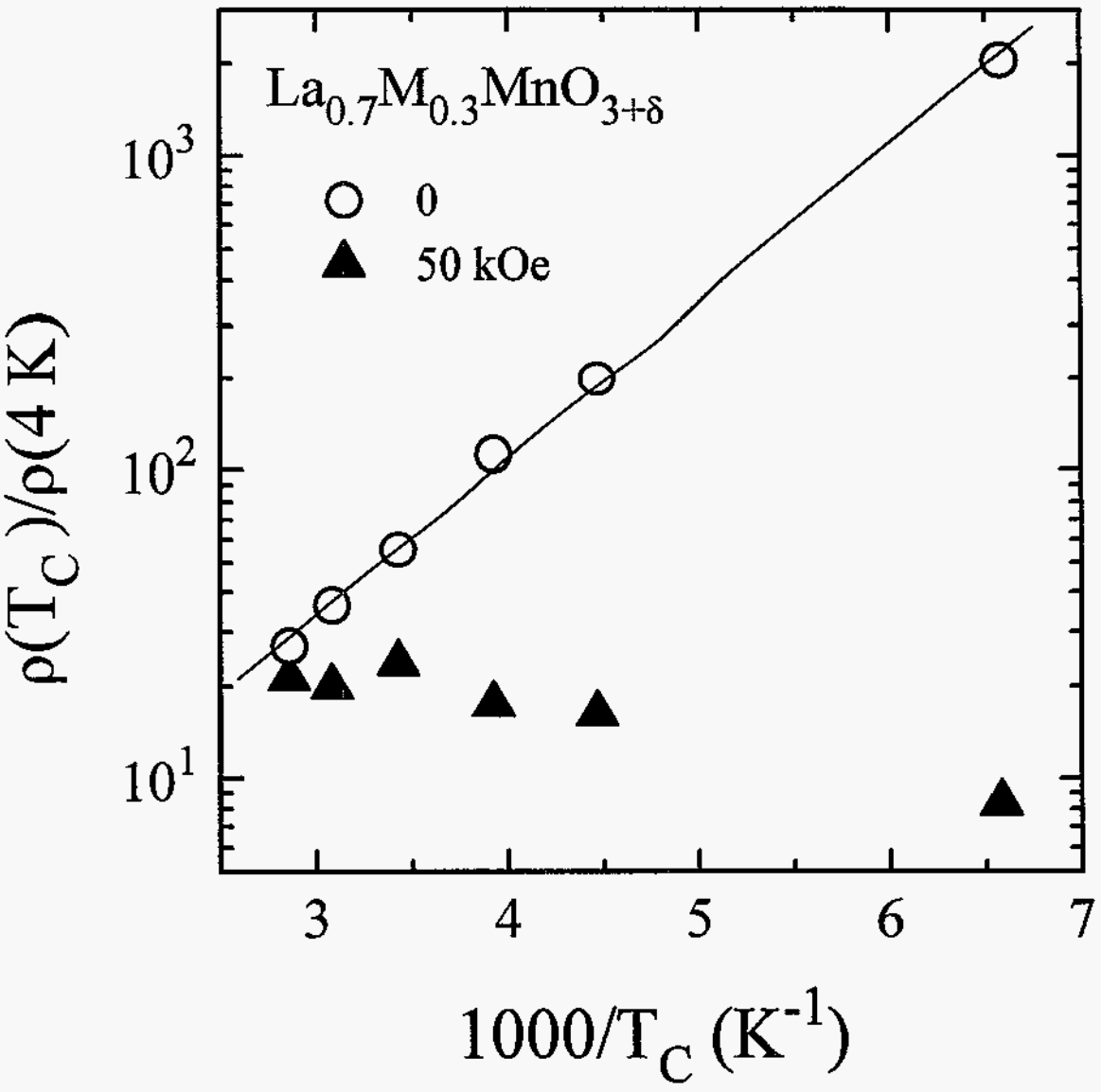
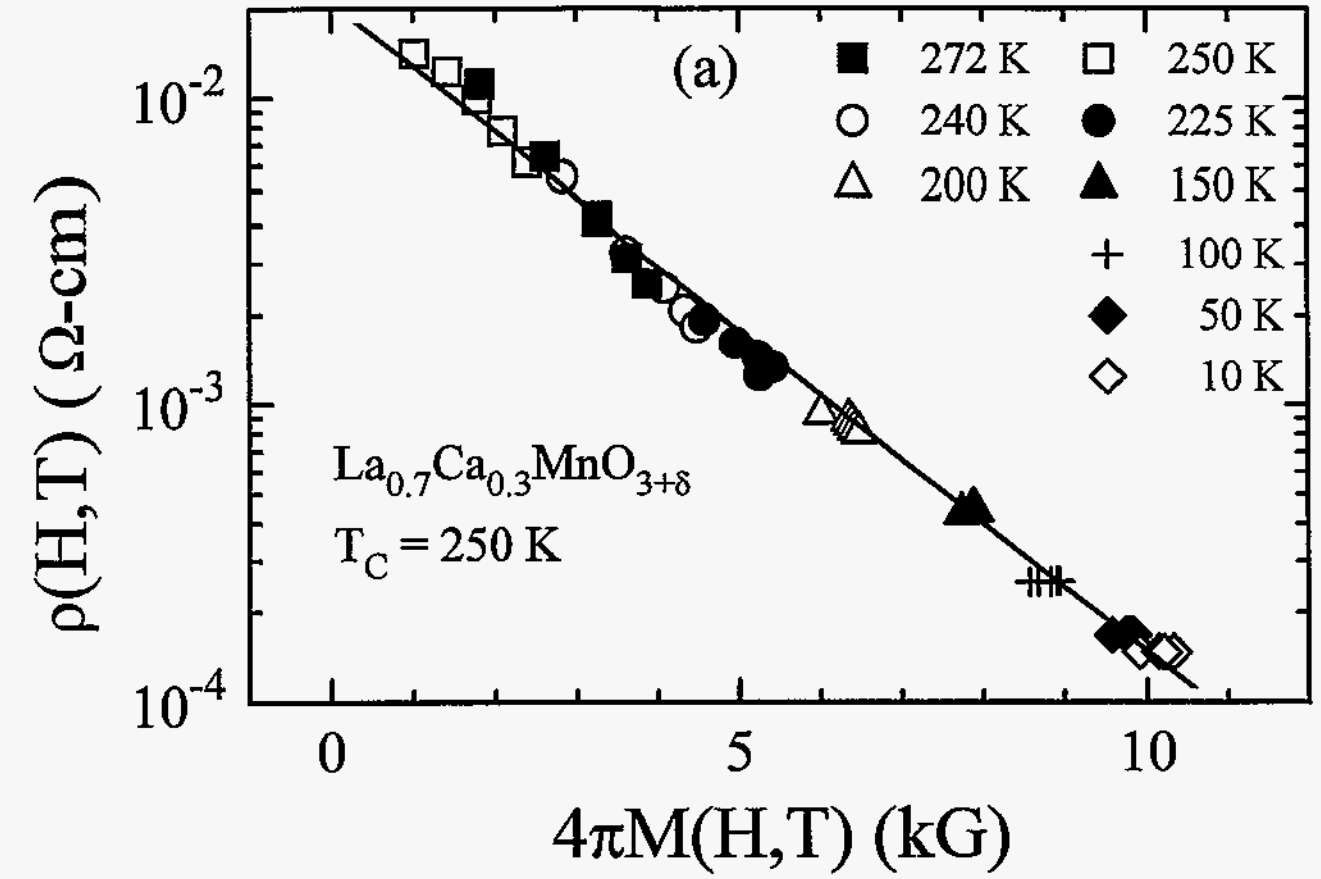


Fig. 3 Hundley et al AC-01



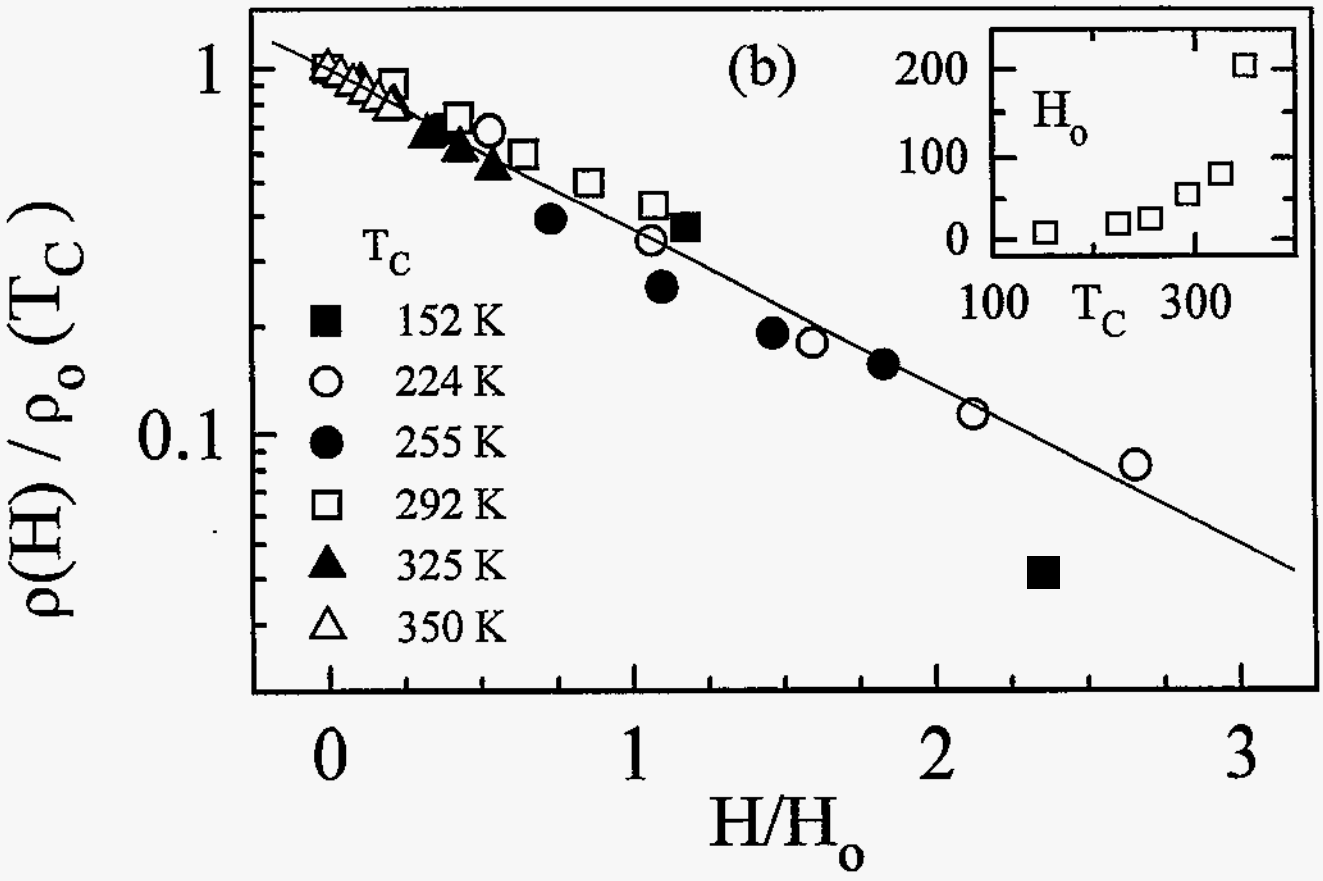


Fig 4 Hundley et al. AC-c