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High-temperature magnetic anomalies in Sr-doped La manganite structures

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High-temperature magnetic anomalies in Sr-doped La manganite structures

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The temperature dependence of the magnetization (M), susceptibility (χ) and magnetoresistance (MR) for three perovskite-variant manganite structures were studied: monoclinic (x=0.075) and orthorhombic (x=0.125) $La_{1-x}Sr_xMnO_3$, and tetragonal layered $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.4) with x also indicating the nominal fraction of Mn^{4+}. In each case evidence is found for unusual magnetic states at temperatures (T) above their primary magnetic transitions. In the first case, the high-T χ deviates from Curie-Weiss expectations, in the second case the MR extends to high T, and in the last, M and χ exhibit short-range anomalies at high T. This suggests that a key feature of these systems is the existence of multiple magnetic energy scales, independent of structure, dimensionality, or doping levels.

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The level of interest in the manganite systems has risen due to the identification that the metal-insulator (MI) transition is field-driven, hence the term colossal magnetoresistance (CMR).[1-3] The origins of this effect are not yet clear. One of the obstacles to a more lucid understanding is the fact that these systems show dynamic interplay between their structural, magnetic and electrical transport properties. Substitution of 2+ cation dopants (e.g. Sr or Ca) in the La^{3+} sites of $LaMnO_3$, for example, can affect all three macroscopic properties, hence it is difficult to sort out which properties are the cause and which are the result of the MI transition and corresponding CMR. For some dopant concentrations simultaneous phase transitions occur in the magnetism, structure and transport.[4] Recently it was reported that the Curie temperature, T_C, can be enhanced by changing the isotopic mass of oxygen.[5] Such sensitivity to the phonon modes indicates that magnetism may well be present at higher temperatures, requiring a change in the phonon spectrum to bring out the long range order.

We present magnetic and electrical transport data for three manganite samples. They are composed of compacted powders of monoclinic $La_{1-x}Sr_xMnO_3$ with x=0.075, an antiferromagnetic insulator with a Neel temperature T_N of 120 K,[6] orthorhombic $La_{1-x}Sr_xMnO_3$, with x=0.125,[7] a canted ferromagnetic insulator with a Curie temperature T_C of 200 K, and a single crystal of tetragonal $La_{2-2x}Sr_{1+2x}Mn_2O_7$ with x=0.4,[8] a quasi-two-dimensional (2D) or layered ferromagnetic metal with a T_C of 120 K. In the following we refer to the samples by their nominal doping x, keeping in mind that the actual Mn^{4+} concentration is higher due to the inevitable presence of

defects. Although these materials show strong lattice effects as the magnetically ordered state is approached, none exhibit structural phase transitions. We find evidence that a secondary magnetic energy scale exists in all samples above their respective primary magnetic transitions identified above by their respective T_C or T_N values. For the x=0.075 sample the inverse susceptibility ($1/\chi$) extrapolation identifies a higher energy scale than $k_B T_N$. For the x=0.125 sample the evidence from neutron scattering is that antiferromagnetic order is retained well above T_C. For the layered material the magnetization remains finite out to more than $2T_C$, but neutron scattering fails to detect long range order.

The structure of these materials was determined by both neutron and x-ray diffraction. Details of both techniques and most of the structural results have been presented elsewhere.[6,7] The x=0.075 sample forms a monoclinic structure ($P2_1/c$) consistent with earlier work in the undoped manganite system.[8] The refinements of neutron diffraction scans indicate that there are four symmetry-independent MnO_6 octahedra all of which are severely Jahn-Teller distorted. The distortion is as large as 13% at room temperature. The x=0.125 sample forms an orthorhombic structure (Pbnm) which also has a Jahn-Teller distortion, however all MnO_6 octahedra are identical and the overall distortion is relatively small (1% at room temperature). The $La_{1.2}Sr_{1.8}Mn_2O_7$ sample is tetragonal (I4/mmm) and is a two-layered variant of the perovskite, specifically the n=2 member of the Ruddlesden-Popper series $(La,Sr)_{n+1}Mn_nO_{3n+1}$.[8] Its MnO_6 octahedra are Jahn-Teller distorted, but with five short and one long MnO bond,

reflecting the mirror symmetry through the middle of the two MnO_6 layers.

The x=0.075 and 0.125 samples display insulating behavior ($d\rho/dT < 0$) as measured below 350 K. The highly doped quasi 2D structure is insulating above T_C=115 K, below which the resistivity sharply drops. Despite the difference in doping levels, it is important to note that the percolation threshold roughly doubles in going from 3D to 2D.[10] Therefore it is not surprising that the x=0.125 sample lies just below the metallic region while $La_{1.2}Sr_{1.8}Mn_2O_7$ lies in the MI region.

The low field R vs. T for the three samples is plotted in Fig. 1. We find that in the high-temperature regime all three samples follow a variable-range hopping law, i.e. ln R vs. $T^{-1/4}$ is linear in the 3D structures, and ln R vs. $T^{-1/3}$ is linear for the 2D layered system. Theoretically variable-range hopping should only persist to $\Theta_D/2$, where Θ_D is the Debye temperature, but is found experimentally to hold to higher temperatures for a number of semiconducting systems.[11] The present systems are complicated by the presence of magnetic correlations above their primary magnetic transition temperatures, thus an additional magnetic energy scale may alter the energy widths with respect to $k_B\Theta_D$.

The resistivity through T_C (centered at 115 K) of the two-layer $La_{1.2}Sr_{1.8}Mn_2O_7$ sample drops sharply by about two orders of magnitude, becoming metallic in the sense that $d\rho/dT > 0$ (although such terminology may be a misnomer since even the single crystal manganites have unusually high resistivities > 1 mΩ-cm). However below about 40 K, R begins to rise as T falls (see Fig. 1c), again

reminiscent of semiconducting behavior. We have seen such low-T behavior in a number of sintered powder samples, however in the present case the behavior is considered intrinsic since the sample is a large single crystal, and thus intergrain effects are not present.

The high-T anomaly in the low-doped material is observed in its susceptibility. Figure 2a shows χ for the insulating antiferromagnet $La_{0.925}Sr_{0.075}MnO_3$. T_N is sharply defined at 120 K, however the high T region of $1/\chi$ does not extrapolate to $-T_N$ as would be expected from Curie-Weiss behavior. In fact an extrapolation yields about +275 K (see inset of Fig. 2a). As seen in Fig. 2b this corresponds to about the T where the MR begins to rapidly rise.

The high-T anomaly in the x=0.125 sample is observed in neutron scattering and corroborated in the MR. Figure 3a shows M and χ for $La_{0.875}Sr_{0.125}MnO_3$. Neutron studies of this material indicate that below T_C = 200 K this system is a canted ferromagnet. However above T_C the z component of the moment vanishes leaving about a one bohr magneton antiferromagnet that persists above room temperature. This is borne out in both the large χ and moment in high field. χ peaks at about 150 K, well below T_C (200 K) or T_N (> 300 K). The MR (Fig. 3b) is substantial up to 350 K, however its peak at 200 K correlates with T_C. The χ peak should indicate a divergence of the magnetic correlation length and thus we would expect χ to be related to the magnetic scattering length. Analysis of the applicability of scaling laws in this problem is needed. Since the system lies near the percolation threshold for metallic-like

conduction such analysis might shed light on the unusual position of the χ peak in relation to both the T_C and the MR peak.

The high-T anomaly for the layered system provides the most compelling example. Figure 4a shows M and χ. The system has two magnetic transitions, the primary one at 115 K and another at 290 K. Neutron scattering results indicate a lack of long range order above 120 K. It was suggested that the higher T behavior may be a manifestation of fluctuations due to the low effective dimensionality of the system.[8] However, such fluctuations should die out exponentially with T, and χ should not be so sensitive to short range correlations. Figure 4b shows that although the MR effect is truly colossal at 5800 %, it is only associated with the long-range order transition centered at T_C = 115 K. The nature of the high-T magnetic state is still not clear.

The overview given here leads to the realization that unlike standard magnetic systems, the manganites show substantial fluctuation effects well above their primary magnetic transitions. The MR does not correlate well with χ, bringing into question ideas about the length scales involved in the magnetization process and electron motion. Recent work on the oxygen isotope effect indicates that the phonon modes are capable of shifting T_C by 20 K,[5] a substantial shift again indicating that magnetism is present at higher T, needing additional phonon coupling to develop long-range correlations. The latter experiment certainly demonstrates the importance of dynamic considerations in a comprehensive understanding of these systems. Given a) the length scales involved in conduction processes and polaron formation, and b) the fact that χ shows such unusual

behavior in samples near the percolation threshold, it seems that further progress in understanding these disordered systems will involve critical scaling behavior as well as a more comprehensive view of the role of dynamic spin-lattice behavior.

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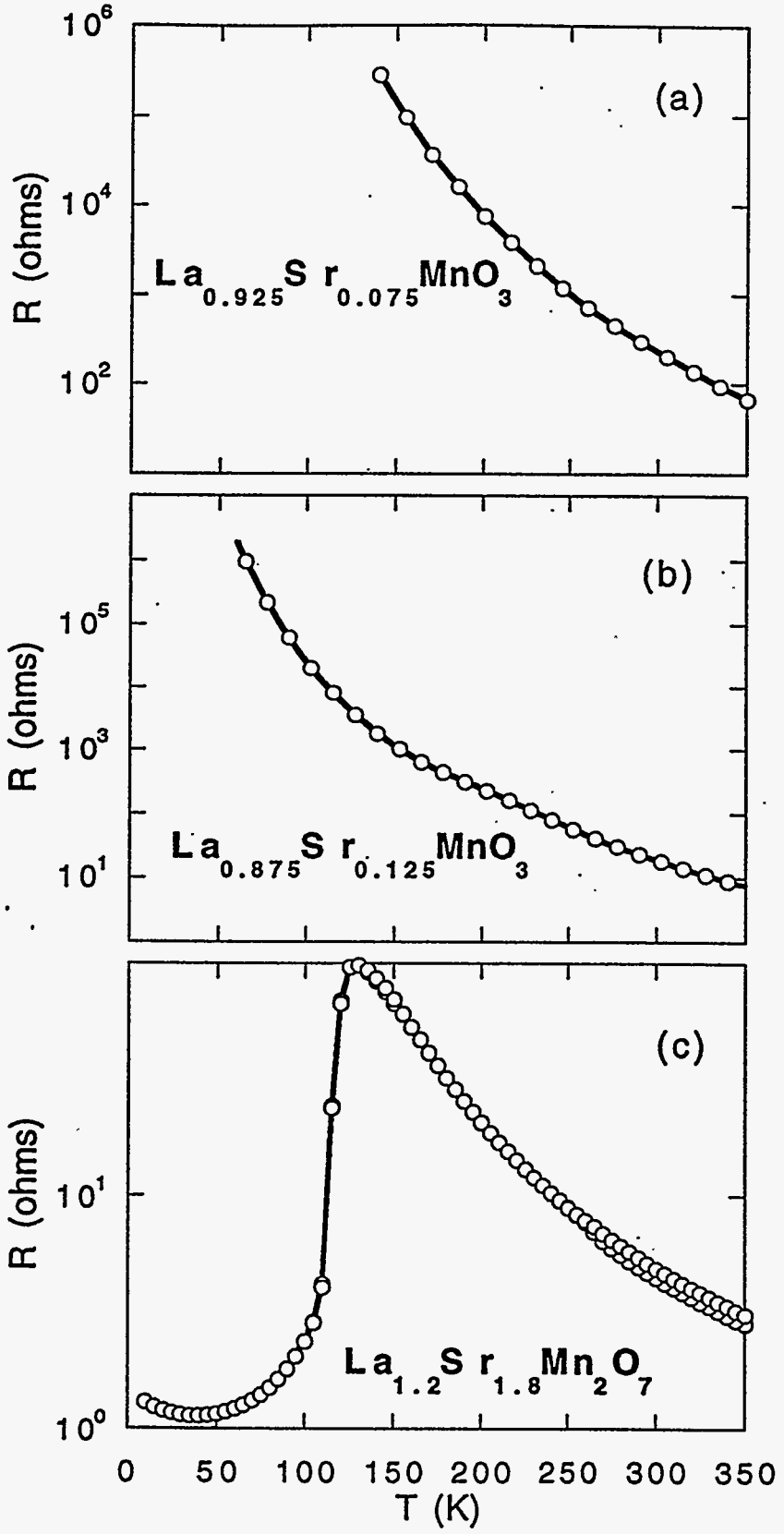
Figure Captions

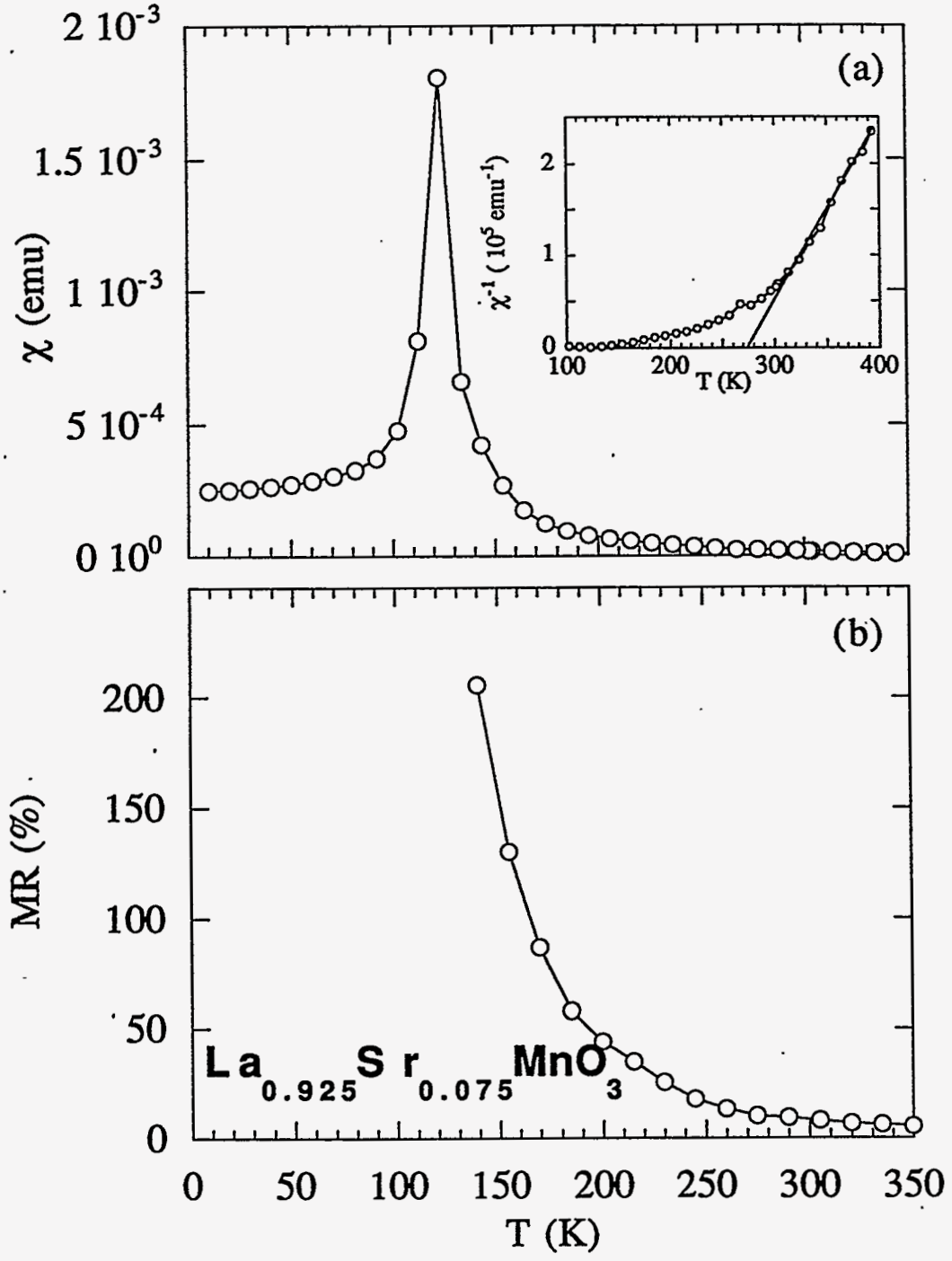
1.) Low field (30 Oe) resistivity vs. temperature for a) $La_{0.925}Sr_{0.075}MnO_3$ b) $La_{0.875}Sr_{0.125}MnO_3$ and c) $La_{1.2}Sr_{1.8}Mn_2O_7$.

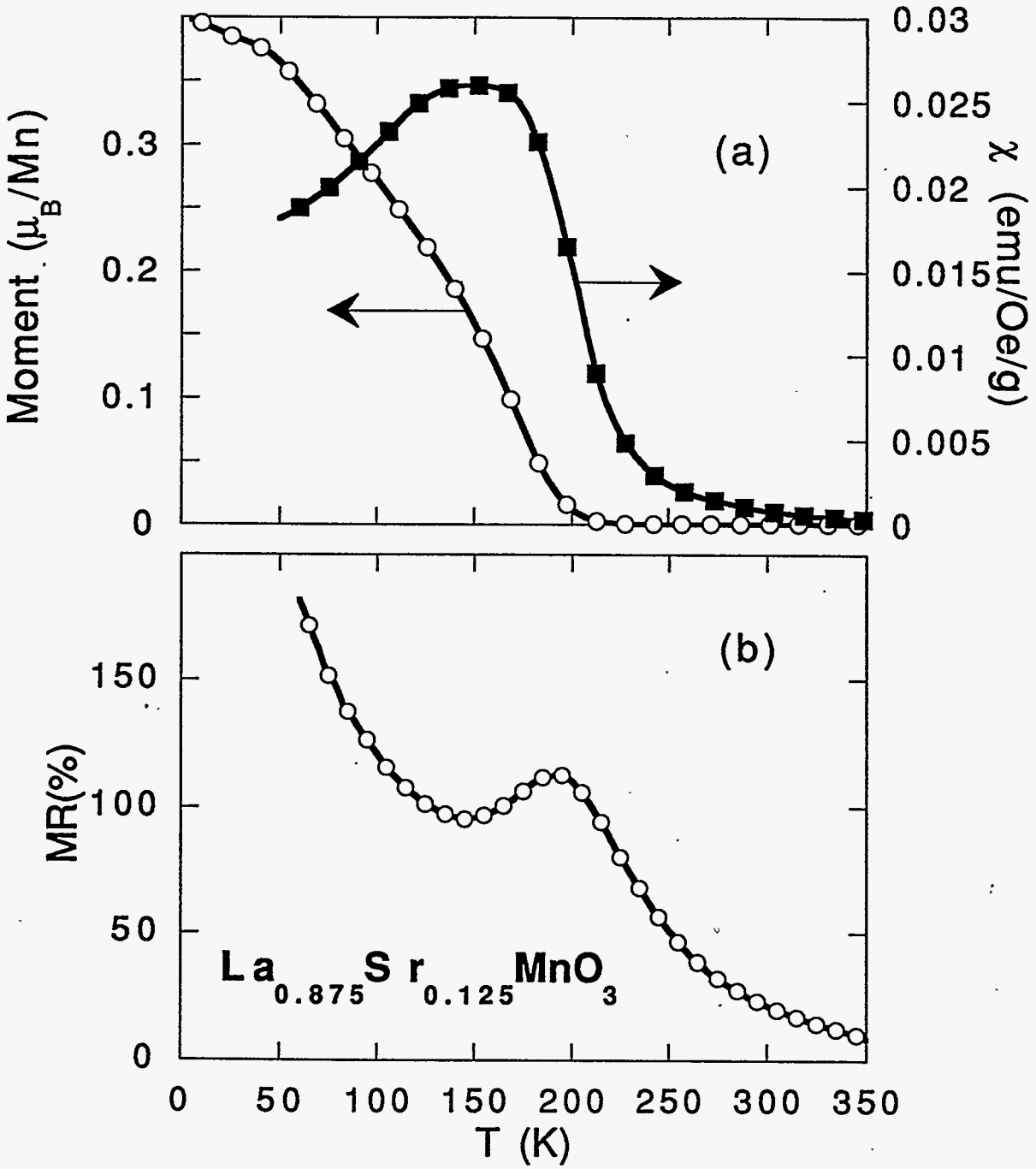
2.) a) Low-field susceptibility, and b) magnetoresistance (% relative to high field) vs. temperature for $La_{0.925}Sr_{0.075}MnO_3$. The inset shows the inverse susceptibility vs. T.

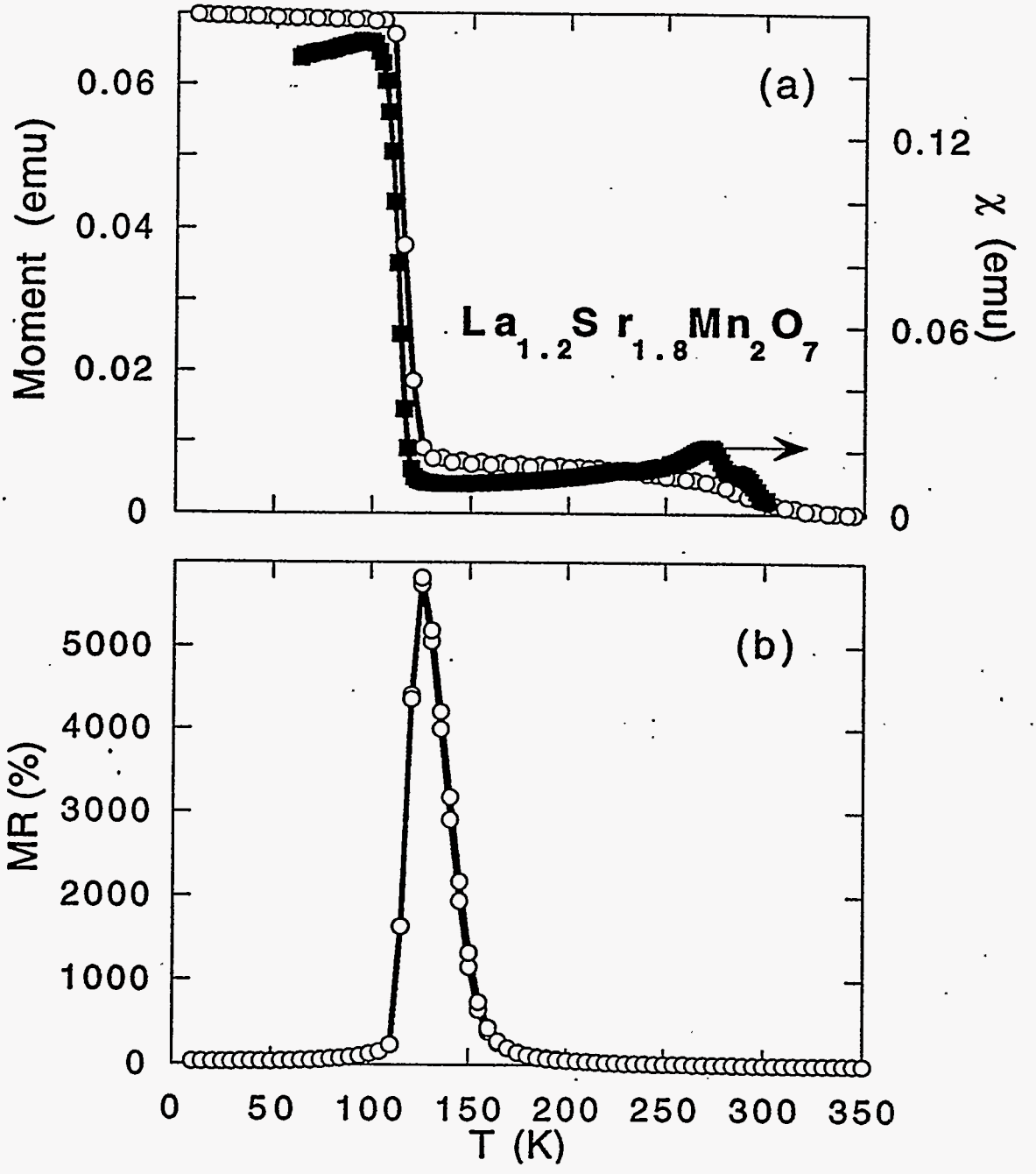
3.) a) Low-field susceptibility and moment, and b) magnetoresistance (% relative to high field) vs. temperature for $La_{0.875}Sr_{0.125}MnO_3$.

4.) a) Low-field susceptibility and moment, and b) magnetoresistance (% relative to high field) vs. temperature for $La_{1.2}Sr_{1.8}Mn_2O_7$.


(a)
R (ohms)
10^6
10^4
10^2
$La_{0.925}Sr_{0.075}MnO_3$
(b)
R (ohms)
10^5
10^3
10^1
$La_{0.875}Sr_{0.125}MnO_3$
(c)
R (ohms)
10^1
10^0
$La_{1.2}Sr_{1.8}Mn_2O_7$
0 50 100 150 200 250 300 350
T (K)


(a)
(b)
χ (emu)
MR (%)
T (K)
χ⁻¹ (10⁵ emu⁻¹)
La0.925Sr0.075MnO3
2 10-3
1.5 10-3
1 10-3
5 10-4
0 10⁰
200
150
100
50
0
0 50 100 150 200 250 300 350
100 200 300 400
2
1
0


Moment (μ_B/Mn)
0.3
0.2
0.1
0
(a)
0.03
0.025
0.02
0.015
0.01
0.005
0
χ (emu/Oe/g)
MR(%)
150
100
50
0
(b)
$La_{0.875}Sr_{0.125}MnO_3$
0
50
100
150
200
250
300
350
T (K)


(a)
Moment (emu)
0.06
0.04
0.02
0
0.12
0.06
0
χ (emu)
La1.2Sr1.8Mn2O7
(b)
MR (%)
5000
4000
3000
2000
1000
0
0
50
100
150
200
250
300
350
T (K)