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


Materials Science Division
and
Science and Technology Center for Superconductivity
Argonne National Laboratory, Argonne, IL 60439

41st Annual Conference on Magnetism and Magnetic Materials, Atlanta, GA, November 12-15, 1996

Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences under contract #W-31-109-ENG-38 and by the National Science Foundation Offices of Science and Technology Center under contract DMR 91-20000 (DNA).

*Present address: University of Illinois, Urbana, IL.
†Present address: Los Alamos National Laboratory, Los Alamos, NM.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
High-temperature magnetic anomalies in Sr-doped La manganite structures

Materials Science Division and §Science and Technology Center for Superconductivity, Argonne National Laboratory, Argonne, IL 60439

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.

* Present address: Univ. of Ill. at Urbana-Champaign.
† Present address: Los Alamos Neutron Science Center, Los Alamos National Laboratory.
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). 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\textsuperscript{3+} sites of LaMnO\textsubscript{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. Recently it was reported that the Curie temperature, T\textsubscript{C}, can be enhanced by changing the isotopic mass of oxygen. 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\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} with x=0.075, an antiferromagnetic insulator with a Neel temperature T\textsubscript{N} of 120 K, orthorhombic La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}, with x=0.125, a canted ferromagnetic insulator with a Curie temperature T\textsubscript{C} of 200 K, and a single crystal of tetragonal La\textsubscript{2-2x}Sr\textsubscript{1+2x}Mn\textsubscript{2}O\textsubscript{7} with x=0.4, a quasi-two-dimensional (2D) or layered ferromagnetic metal with a T\textsubscript{C} of 120 K. In the following we refer to the samples by their nominal doping x, keeping in mind that the actual Mn\textsuperscript{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/χ) 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. The x=0.075 sample forms a monoclinic structure (P2_1/c) consistent with earlier work in the undoped manganite system. 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+1Mn_nO_{3n+1}. 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$_2$O$_7$ 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 $\Theta_D$ 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$_2$O$_7$ 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 $> 1$ m$\Omega$-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 $\chi$ 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 $\chi$ 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 $\chi$ and moment in high field. $\chi$ 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 $\chi$ peak should indicate a divergence of the magnetic correlation length and thus we would expect $\chi$ 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
condensation such analysis might shed light on the unusual position of the \( \chi \) 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 \( \chi \). 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. However, such fluctuations should die out exponentially with T, and \( \chi \) 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 \( \chi \), 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, 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 \( \chi \) 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.

Work supported by the U.S. Dept. of Energy, BES-MS and ER-LTR under contract W-31-109-ENG-38 and by the NSF OSTC under DMR 91-20000 (DNA).
References


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$_2$O$_7$.

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$_2$O$_7$. 