First-Order Metal-Insulator Transitions in Manganites: Are They Universal?

Qing’ An Li*
Chinese Academy of Sciences, Beijing, China, and Materials Sciences Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

Materials Sciences Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
(Received 29 November 2005; published 28 February 2006)

Conductivity data for La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ ($x = 0.6$) show a first-order transition from an orbital- or charge-ordered insulator to a metal as the temperature falls below $\sim 160$ K. The change in conductivity is 100 times larger than that seen previously in any single-phase manganite in zero field. The metallic low-temperature state is similar to $x = 0.58$, but $x = 0.58$ shows no evidence of orbital or charge order. This result supports a conclusion that strongly coupled magnetic-conductive transitions are first order.

DOI: 10.1103/PhysRevLett.96.087201
PACS numbers: 75.30.Et, 75.60.-d

In studies of colossal magnetoresistance [1] (CMR), doped bilayered manganites, La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$, exhibit a particularly rich phase diagram [2,3] and advantages for investigating the correlation among spin, charge, lattice, and orbital degrees of freedom [4]. Metallic conduction, which accompanies ferromagnetic (FM) order, can be understood in terms of the double-exchange (DE) theory [5] that is well established experimentally [6]. In DE, conduction is enhanced for neighboring spins that are parallel and suppressed for antiferromagnetic (AFM) alignment.

It was pointed out early on [7] that DE alone is not enough to explain the CMR effect and some kind of electron localization mechanism is needed for the high-temperature paramagnetic insulating phase. However, electron localization also occurs below the magnetic ordering temperature. For example [8–11], CE-type orbital or charge order is found below $\sim 200$ K in the $x = 0.5$ layered manganite although it commonly transforms [9–11] into an A-type AFM (AAFM) insulator below $\sim 100$ K. The generic AAFM spin arrangement exhibits AFM alignment between FM monolayers of the bilayer [3,12]. The low-temperature AAFM insulator for [13] $x = 0.48$ and [14] $x \sim 0.5$ needs a localization mechanism since DE theory predicts [15] and experiments for $x = 0.58$ confirm [16] a metallic ground state in the FM monolayers below $\sim 200$ K.

We report here an in-plane metallic ground state in the FM monolayers below $\sim 160$ K in the bilayer manganite for $x = 0.6$. A novel feature is the clear demonstration of a first-order transition from an orbital- or charge-ordered insulator into an $ab$-plane metal that occurs in zero magnetic field. Between 160 and 250 K, there is a distinctive, considerable decrease in the conductivity below that of the high-temperature paramagnetic insulator that is consistent with the occurrence of the previously reported bistripe (BIS) orbital- or charge-ordered state [17–20].

For $x = 0.6$, Fig. 1 shows that $\sigma_{ab}(T)$ and $\sigma_{c}(T)$ are qualitatively similar to $x = 0.58$ at low temperatures. However, for $x = 0.58$, $\sigma_{ab}$ is at least 10 times smaller and there is no evidence of orbital or charge order. Unexpectedly, the low-temperature $ab$-plane conductivity, $\sigma_{ab}$, is considerably higher than any bilayered manganite.
reported to date including the FM, metallic compositions \((x = 0.32 \text{ to } -0.42)\). The inset of Fig. 1(c) shows the magnetization, \(M\), of the same crystal (A) used for conductivity and x-ray diffraction and a second crystal (B) from the same boule. Crystal B exhibits the BIS state over a narrower temperature range. This may be due to an average \(x\) value farther from the ideal, commensurate value of 0.6, thus making the BIS state less stable compared to the paramagnetic insulator and low-temperature metallic states.

Crystals were meltgrown \([21]\) in an optical image furnace. The \(c\) axis is perpendicular to the platelike crystals \((2 \times 0.5 \times 0.1 \text{ mm}^3)\) and four gold pads are deposited along the top and bottom surfaces. Then one can determine \([14,22]\) each component of conductivity, \(\sigma_{ab}\) and \(\sigma_c\), and test the crystal homogeneity \([22]\). In method A \([\text{Fig. 1(a)}]\), current is injected through the outermost contacts on one surface. Voltages are measured across the innermost contacts of each surface and Laplace’s equation is solved and inverted to get \(\sigma_{ab}\) and \(\sigma_c\). Alternatively, method B \([\text{Fig. 1(b)}]\) solves Laplace’s equation for the current injected through the top and bottom contacts at one end of the crystal, while the voltages are measured between two other sets of corresponding contacts on the top and bottom of the crystal. The agreement between these has been used as a test of homogeneity in previous studies \([22]\).

For method A on the highly anisotropic \(x = 0.6\) sample, the voltages on the opposite face are too small to be reliable. Thus, we use the Laplace solution in method B for a reliable determination of \(\sigma_c\). Then using that \(\sigma_c\), together with voltages from the innermost contacts on the same face to current injection of method A, Laplace’s equation can be solved for the single unknown, \(\sigma_{ab}\). We average the values over the various contact permutations to yield the results shown in Fig. 1(c). For \(T > 250\text{ K}\) the data closely resemble the behavior of all other compositions we have measured \([6,13,16,22–24]\); e.g., see the data for \(\sigma_{ab}\) at \(x = 0.36\) in Fig. 1(c). This includes an excellent fit to a single thermal activation energy \((\sim 1600\text{ K here})\) for \(\sigma_c\) and a weaker dependence for \(\sigma_{ab}\) due to in-plane FM fluctuations \([25]\). The behavior below 250 K is novel and it corresponds to the BIS phase noted previously by scattering probes \([18–20]\).

Between 175 and 150 K there is an abrupt, huge change \((\sim 10^4)\) in \(\sigma_{ab}\) into a metallic state at low temperatures. The low-temperature values of \(\sigma_{ab}\) are significantly larger than any bilayer manganite studied previously. The sharpness and hysteresis strongly implies a first-order transition from a metal (AAFM) to a long-range orbital- or charge-ordered insulator (BIS), and we believe this to be the first report of such a transition in zero magnetic field in a single-phase CMR material. The increase in \(\sigma_c\) is smaller than \(\sigma_{ab}\), consistent with a suppressed \(\sigma_c\) due to the antiparallel orientation along the \(c\) axis of the AAFM. At the lowest temperatures, \(\sigma_c\) is approximately linear in \(T\); this dependence is consistent with that of the \(c\) axis AFM layered manganites at \(x = 0.3\) and \(x = 0.58\), which was explained \([6,16]\) by spin-wave fluctuations spoiling the perfect AFM order along the \(c\) axis. In the (shaded) transition region, the features in the data reflect a slight inhomogeneity in composition and thus transition temperature, which is amplified by the \(10^4\) change in \(\sigma_{ab}\).

The effects of slight compositional inhomogeneity can be serious when properties vary strongly with \(x\), so we have carefully evaluated this by measuring \(\sigma_{ab}\) and \(\sigma_c\) for all four principal current injection configurations. Two of these use method A with the current applied through the outer contacts on either the top or bottom surfaces and two use method B with the current applied through the end contacts on either the right- and left-hand sides of the crystal. These \(\sigma_{ab}\), shown in Fig. 2, give virtually identical results in the insulating phases above 175 K. Below 150 K, they vary by about a factor of 3 with considerable noise for method A due to the large anisotropy (>60,000 at the lowest \(T\)). Thus the exact magnitude of \(\sigma_{ab}\) is less certain, but it clearly exhibits metallic values. The peaks and dips near the transition at \(\sim 160\text{ K}\) are due to distorted current paths arising from slightly different \(T_C\) (i.e., \(x\)) values within the crystal.

Orbital order results in a superlattice reflection that confirms the presence of the BIS state. High-energy x-ray diffraction images \([26]\) on the same crystal used for transport are shown in the inset of Fig. 2. New superlattice peaks appear at \((h \pm \delta, \pm \delta, 0)\) for several \(h\) values when \(T = 165–225\text{ K}\) that were missing at room temperature and at 145 K. The superlattice peak position (\(\delta = 0.21\)) is within

![Graph](image-url)
the range of other reports [18–20] for \( x = 0.6 \). The intensity of the \((2.21, 0.21, 0)\) peak is plotted in Fig. 2, and its gradual change around 155 to 165 K is entirely consistent with smearing of the first-order metal-insulator transition (MIT) due to the slight inhomogeneity in \( T_C \) noted above.

The low-temperature behavior of \( \sigma_{ab} \) and \( \sigma_c \) is shown in Fig. 3 on a linear scale. As \( T \) approaches zero, both \( \sigma_{ab} \) and \( \sigma_c \) are in sharp contrast to the stronger, quasieponential dependence shown for the insulating compounds \([14,23]\) near \( x = 0.5 \). Instead, the finite zero-temperature intercept of \( \sigma_{ab} \) implies metallic behavior, although it does exhibit a slight drop at lowest temperatures that is a characteristic of the bilayer manganites (see also \( \sigma_{ab} \) for \( x = 0.36 \) in Fig. 3) and ascribed to weak localization effects \([24,27]\). Applied fields had little effect on the conductivity: at 10 K the maximum change was a few percent at 5 T, while a slight increase in the transition temperature (\(~3–4\) K at 7 T) was found near the MIT at 160–170 K. The weak response to fields implies a relatively strong AFM superexchange that reduces the susceptibility, consistent with the magnetization, \( M_s \), shown at 3 T in Fig. 1(c) (inset). The CMR effect near the MIT was not studied in detail due to the effect of slight inhomogeneity noted above.

The lack of significant hysteresis in \( \sigma \) and \( M \) in previously measured bilayer manganites could be taken as evidence for a second-order MIT. However, a question is whether extended Bloch states in a metal can evolve continuously into the localized states of an insulator. The tight-binding approximation suggests a continuous transition from a metal to isolated atoms as the interatomic distance is continuously increased. However, by including the Coulomb interaction, an abrupt drop to the insulating state (i.e., a Mott transition) is expected \([28]\). Double exchange \([5]\) allows one to tune the wave function overlap through the relative spin orientation of neighboring Mn ions without significantly changing the interatomic distance. The bilayer manganite with \( x = 0.48 \) is an example of a first-order MIT as a function of magnetization, induced by an applied field \([13]\). The intimate connection of \( \sigma \) and \( M \) in DE may cast doubt on any analysis in terms of a single order parameter, and may make a continuous transition (necessarily with two order parameters) more problematic.

An example of a first-order MIT as a function of temperature is found \([29]\) in the perovskite manganite, \( \text{La}_0.7 \text{Ca}_0.3 \text{MnO}_3 \) (i.e., \( x = 0.3 \)). Support for a second-order transition is found in the scaling behavior \([25]\) of the fluctuation magnetization above \( T_C \) in the layered manganite with \( x = 0.4 \). However, the fairly abrupt change in the spontaneous magnetization just below \( T_C \) (inset of Fig. 4 of Ref. \([25]\)), which implied an anomalously low value for the critical exponent, \( \beta \), may be an indication that it is really a first-order coupled magnetic MIT superseding the purely magnetic transition. The metallic delocalization of electrons enables DE (i.e., enhances the FM coupling constant, \( J \), above that of the insulator) with a concomitant increase of the magnetic ordering temperature (\( T_C \sim J \)) above that intuited from the high-temperature magnetic fluctuations.

The textbook scaling of the magnetization in \( \text{La}_{0.8} \text{Sr}_{0.2} \text{MnO}_3 \) is clear evidence of a second-order magnetic transition \([30]\), but not necessarily a MIT at \( T_C \). It can be argued that magnetic order enhances thermally activated hopping below \( T_C \) by lowering the Hund rule energy cost. The detailed \( T \) dependence of the measured conductivity \([30,31]\) can be fit convincingly, from \( T_C \sim 305 \) K down to \(~150\) K, by the function \([32]\)

\[
\sigma(T) = \sigma_s \exp\left(-\left(T_{\text{hop}}(0) + T_{\text{hop}}[1 - M(T)/M_s]\right)/T\right),
\]

(1)

where the second term, with \( T_{\text{hop}} = 1700 \) K, is a disorder potential, as in Anderson localization, that is due to Hund’s rule and vanishes for FM spin order. \( T_{\text{hop}}(0) \sim 50 \) K and \( M(T)/M_s \) is measured \([30]\). This line of reasoning is analogous to the CMR effect above \( T_C \), for which an applied field induces an average \( M \) and a colossal enhancement of conductivity \([32]\) without a MIT. We have tested Eq. (1) on \( \sigma(H) \) above \( T_C \), as a function of the measured \( M(H) \), for bilayer manganite crystals with \( x = 0.32 \) (see Fig. 7 of Ref. \([13]\)) and 0.4. These fits are convincing, and the values of \( \sigma_s \) and \( T_{\text{hop}} = 1300 \) and 1150 K, respectively, are in excellent agreement with fits of the measured \( \sigma(T) \) to \( \sigma_s \exp\left[-T_{\text{hop}}/T\right] \) in zero field (i.e., \( M = 0 \)). Thus there is a consistent picture of \( \text{La}_{0.8} \text{Sr}_{0.2} \text{MnO}_3 \) in which there is only a magnetic transition at \(~305\) K. Below \(~100\) K, \( \sigma(T) \) is significantly greater than Eq. (1) predicts, thereby giving evidence of a MIT near \( 100–150 \) K.
Thus, as it seems reasonable to see a first-order MIT, one asks why it is not clearly seen for the metallic bilayer manganites \((0.31 < x < 0.46)\). One possibility is that due to the hundredfold smaller conductivity difference, between the metal and the high-temperature paramagnetic insulator [see Fig. 1(c)], the first-order MIT is smeared out by a small compositional inhomogeneity.

In summary, we present clear evidence for a first-order transition from a charge or orbital ordered insulator to an in-plane metal at low temperatures in the layered manganite with \(x = 0.6\). This appears to be the first example of such a transition in any single-phase manganite in zero field. Nevertheless, our result and analysis support the premise that strongly coupled magnetic-conductive transitions may be universally of first order. We also note that our results point to the conclusion that orbital or charge-ordered states are restricted to narrow compositional ranges near to \(x = 0.5\) \((CE)\) and \(x = 0.6\) \((BIS)\) in layered manganites.

The authors thank Peter Lee for assistance with synchrotron x-ray diffraction. This research was supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract No. W-31-109-ENG-38.

*Present address: State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, China.


[26] Data were collected with a CCD using high-energy synchrotron x rays at the 1-ID beam line of the Advanced Photon Source, Argonne National Laboratory.


