Distinct insulating state below the Curie point in Pr$_{0.7}$Ba$_{0.3}$MnO$_3$

A. K. Heilman, 1 Y. Y. Xue, 1 B. Lorenz, 1 B. J. Campbell, 2 J. Cmaidalka, 1 R. L. Meng, 1 Y. S. Wang, 1 and C. W. Chu 1,*

1Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5932
2Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 5 November 2001; revised manuscript received 6 March 2002; published 5 June 2002)

Magnetization, resistivity, thermal expansion, expansion, thermopower, and neutron powder diffraction data are presented for the perovskite manganite Pr$_{0.7}$Ba$_{0.3}$MnO$_3$. A distinct ferromagnetic insulating state, similar to that observed in the La$_{0.88}$Sr$_{0.12}$MnO$_3$ system, is observed in the temperature range between the paramagnetic-ferromagnetic transition at $T_F = \approx 180$ K and the broad metal-insulator transition near $T_p = 120$ K. The large A-site cation-size mismatch appears to suppress the ferromagnetic double-exchange interactions relative to the competing ferromagnetic superexchange interactions, thereby giving rise to the ferromagnetic insulating state.

DOI: 10.1103/PhysRevB.65.214423

I. INTRODUCTION

The physics responsible for the colossal magnetoresistance (CMR) in the manganites of the form $A_1-xA'_xMnO_3$ (with $A' =$ trivalent rare-earth cation and $A =$ divalent cation) is still a topic of debate in spite of the recent intense research activity. 1 In the framework of the widely accepted double-exchange (DE) mechanism with the Jahn-Teller (JT) distortion, 2,3 the resistivity is dominated by the carrier-hopping rate between the adjacent Mn sites. Thus, the decrease in scattering due to the ordering of the Mn $3d$ spins below the ferromagnetic (FM) transition temperature, $T_F$, causes a drop in $\rho$. In particular, $T_F$ should be coincident with the peak temperature of the resistivity $T_p$ if the sample is an insulator above $T_F$. This has been confirmed in manganites with small A-site cation mismatches. 4 $\sigma^2 = \Sigma y_i \rho_i^2$, $\langle r_A \rangle^2$ (where $y_i$ is the concentration, $r_i$ is the ionic radius of the A-site ions, and $\langle r_A \rangle$ is the mean ionic radius). 1 However, in manganites with large $\sigma^2$, it has been reported that $T_p$ systematically drops below $T_F$ with increasing $\sigma^2$ over a broad range of $\sigma^2$. 4-9 The presence of minor impurity phases/grain boundaries, 4,9 a carrier-localization due to disorder, 5,10 and mesoscopic chemical inhomogeneities (e.g., conducting La-Ca-Mn-O with embedded insulating Gd-Ca-Mn-O) 7 have all been invoked to explain this separation of $T_p$ and $T_F$. Some manganites with large $\langle r_A \rangle$ and $\sigma^2$ have also been reported to exhibit a spin-glass insulating (SGI) state at low temperatures. 6 To explore these issues surrounding the large $\sigma^2$ manganites, high-quality ceramic samples of Pr$_{0.7}$Ba$_{0.3}$MnO$_3$ (PBMO) were synthesized, which possess a strong lattice disorder ($\sigma^2 \approx 0.0178$ Å$^2$, $\langle r_A \rangle = 1.266$ Å) due to the large size difference between the Pr$^{3+}$ and the Ba$^{2+}$ ions. No secondary phases were detected by x-ray diffraction or energy dispersive x-ray.

Several key results are presented in this work. (1) There exists a 60 K temperature difference between $T_F$ ($\approx 180$ K) and $T_p$ ($\approx 120$ K). (2) There are distinct anomalies in the thermal expansion coefficient ($\alpha$) both at $T_F$ and near $T_p$. (3) The thermoelectric power ($S$) and resistivity ($\rho$) both indicate activated carrier-transport above $T_p$ and metallicike transport below $T_p$. The activation energy between $T_F$ and $T_p$ is rather different from those observed above $T_F$. (4) An anomalous drop in the low-field field-cooled magnetization ($M_{FC}$) occurs with cooling across $T_p$. (5) A large magnetoresistance (MR) is observed over a wide temperature range that extends below both $T_F$ and $T_p$. All these are rather different from those observed in a Pr$_{0.7}$Sr$_{0.3}$MnO$_3$ (PSMO) sample with a smaller $\sigma^2 = 0.0036$ Å$^2$ ($\langle r_A \rangle = 1.218$ Å). (6) Neutron diffraction data of PBMO reveal a broad structural phase transition near $T_p$ in addition to the PM-to-FM transition at $T_F$. These data can be interpreted as evidence of two distinct FM states below $T_F$ in the PBMO sample: a ferromagnetic-metallic state (FMM) and a ferromagnetic-insulating state (FMI), similar to those recently observed in La$_{0.88}$Sr$_{0.12}$MnO$_3$, 11 which are proposed to be the result of competition between the DE and super-exchange (SE) interactions.

II. EXPERIMENT

Ceramic samples of Pr-Ba(Sr)-Mn-O were prepared by solid-state reaction of powders of Pr$_6$O$_{11}$, SrCO$_3$, BaCO$_3$, and MnO$_2$ with the stoichiometric compositions. These were ground and die pressed into pellets before preliminary reactions in air at 900–1000 °C for 16 h. The samples were then reground and heated at 1100 °C, 1200 °C, and 1250 °C for 16 h in air and finally slow cooled to room temperature.

The composition of the PBMO sample was analyzed using a JEOL JXA 8600 electron microprobe. A stoichiometry Pr:Ba:Mn:O = 0.69:0.302:1:3.04 with a spread of ± 2% for the cations and ± 5% for the oxygen was observed over the whole surface of the sample. These measurements allow us to conclude that the sample is homogeneous to the length scale of 1 µm. The PSMO sample exhibits a comparable degree of homogeneity. Measurements of $M_{FC}$ and $\rho$ were made simultaneously inside a quantum design superconducting quantum interference device magnetometer, $S$ was measured using an apparatus previously described in detail in Ref. 12, and $\alpha$ was measured using the strain-gage technique. The value of $\rho$ was measured by the standard four-load technique, employing a model LR-400 bridge by Linear Research, Inc. Time-of-flight neutron powder diffraction (NPD) measurements were conducted from 10 K to 300 K on the SEPD instrument at the Argonne National Laboratory Intense Pulsed Neutron Source. Rietveld structure refinements employed the GSAS software suite. 13

0163-1829/2002/65(21)/214423(5)/$20.00 65 214423-1 ©2002 The American Physical Society
III. RESULTS AND DISCUSSION

The $M_{\text{FC}}$ data in applied magnetic fields of 0.1, 1.0, and 3.0 T are shown in the inset of Fig. 1. The temperature inflection point is taken as the PM-to-FM transition temperature ($T_{\text{FM}}=180$ K at 0.1 T). The corresponding field-dependent $\rho$ is shown in Fig. 1, where the peak resistivity at a zero applied field occurs at a temperature $T_{\text{FM}}=120$ K, which is well below $T_{\text{FM}}$. At zero applied field, $\rho$ shows activated transport behavior, $\rho \propto \exp[\Delta/T]$ both above $T_{\text{FM}}$ and between $T_p$ and $T_{\text{FM}}$. There is, however, a noticeable anomaly in $\rho$ near $T_{\text{FM}}$, which appears to be smeared out with increasing field.

A significant MR is observed over a large temperature range extending well below $T_p$, in contrast to typical CMR systems in which the MR is strongly peaked at $T_{\text{FM}}$ and negligible deep in the ferromagnetic-metallic region. The spins of PBMO, however, are well-aligned below $T_{\text{FM}}$, as indicated by the quick saturation of $M$ with cooling at $H \approx 1$ T in Fig. 1. In fact, the $M_{\text{FC}}$ at 1 T reaches 2.5 $\mu_B$/Mn at 150 K, comparable with both the value ($\approx 3$ $\mu_B$/Mn) observed at 10 K and the saturation moment ($\approx 3.7$ $\mu_B$/Mn) expected for typical manganites at this doping level. No significant MR, therfore, would be expected around the much lower temperature $T_{\text{FM}}=0.65T_{\text{FM}}$ based on the DE models. In addition, there are no recognizable $\rho$ versus $M$ correlations, which would be characteristic of spin scattering. The decrease of $\rho$ with $H$ at 50 K, for example, is almost the same either from 0 to 1 T or from 1 to 3 T, although the corresponding increases of $M$ differ by more than tenfold (Fig. 1). All these suggest that factors other than the average spin alignment also play a role. It should be pointed out that the observed onset of the FM moment at $T_{\text{FM}}$, the quick saturation of $M$ with both cooling and magnetic field, the temperature dependence of $\rho$, and the strong MR between $T_{\text{FM}}$ and $T_p$, are also inconsistent with an SGI state, such as that reported in Ref. 6.

The separation of $T_p$ and $T_{\text{FM}}$ has been previously observed in several different high $\sigma^2$ manganites, for example, Nd$_{0.7}$Ba$_{0.3}$MnO$_3$, Th$_{0.35}$(Ba$_{0.75}$Sr$_{0.25}$)MnO$_3$, and $(La_{1-x}Gd_x)_{0.7}$Ca$_{0.3}$MnO$_3$. The large size-mismatch in these compounds makes chemical phase separations, i.e., insulating grain boundaries and/or mixed phases, a strong possibility. Therefore $S$, which is regarded as a volume-average measurement and is insensitive to both grain boundaries and minor impurities, has been determined in zero field and is shown in Fig. 2. The $|S|$ of low $\sigma^2$ manganites, such as PSMO, near the optimal doping level is usually large (10 $\mu$V/K or larger) and insulatorlike with a 1/T dependence above $T_{\text{FM}}$, but drops immediately across the transition before reaches a plateau of a few $\mu$V/K at lower $T$. The $S$ of PBMO does follow the rule above $T_{\text{FM}}$, indicative of activated polaron transport. It, however, jumps to an even negative value with cooling across $T_{\text{FM}}$, indicating that the sample is still in a bulk insulating state (likely also dominated by polaron transport) between $T_{\text{FM}}$ and $T_p$ with an even larger activation energy. The distinguishable insulatorlike $S$, both above and immediately below $T_{\text{FM}}$, confirms that the bulk of PBMO is still in an insulating state somewhere below $T_{\text{FM}}$. The expected transition to a metallic $S$ is rather broad and does not finish until well below $T_p$, a fact attributed to a phase separation between $T_{\text{FM}}$ and $T_p$, as demonstrated in the NPD data below.

Above $T_p$, the NPD data yield a crystal structure with $Ibm\!m$ symmetry as reported by Jirak et al. for high-temperature Pr$_{0.68}$Ba$_{0.32}$MnO$_3$, which has been equivalently described in the $Imma$ setting for a number of other $A_{0.7}A_{0.3}$MnO$_3$ systems. The $Ibm\!m$ setting should be assumed throughout the present work unless otherwise noted.
FIG. 3. Neutron powder diffraction data from PBMO at 10 K. Both the data and the difference curve from the Rietveld refinement of the two-phase model are shown. The top and bottom rows of markers indicate Ibmm and I4/mcm peak positions, respectively. The inset contains the temperature dependence of the (220, 004) peak pair.

While somewhat unusual, the relation $b < a$ observed here indicates a Mn-O-Mn bond angle that varies slightly from 180°. After correcting this relation, which was difficult to resolve in earlier NPD data, one finds our room-temperature Pr$_{0.7}$Ba$_{0.3}$MnO$_3$ lattice parameters $[a = 5.5294(1)$ Å, $b = 5.5001(1)$ Å, $c = 7.7725(1)$ Å] to be nearly identical to those of Ref. 16. Near $T_p$, the NPD data reveal a phase transition to a low-temperature structure with I4/mcm symmetry, which only goes to 75% completion down to the lowest temperatures measured (10 K), producing a mixed-phase region over all the temperature range explored below $T_p$. This structural transition is also hysteretic, occurring primarily between 90 K and 130 K on warming and between 70 K and 110 K on cooling. The results of the Rietveld refinement at 10 K are shown in Fig. 3 and the temperature-dependent lattice-parameters appear in Fig. 4. The (220/004) peak pair is shown as a function of temperature in the inset of Fig. 3, where the smaller (004) peak moves from the left- to the right-hand side of the plot due to the reversal of $c$ and $(a + b)/2$ in the low-temperature I4/mcm phase. The lattice parameters of the Ibmm phase display a weaker peak at $T_{FM}$. The refined FM moment rises to 3.7 $\mu_B$/Mn between $T_{FM}$ and $T_p$, as expected, and lies along the $c$ axis of the structure. In the mixed-phase region, however, the resolution of the data was insufficient to properly treat the FM moments of the two phases separately, so the moments were constrained to be equal and directed along the $c$ axis. No significant JT distortions were observed in the Ibmm or I4/mcm structures, which differ primarily in their octahedral-tilt patterns. This may be closely associated with the good size match between (Pr, Ba) and Mn.

The ceramic thermal-expansion coefficient measurements in Fig. 2 corroborate the NPD observations, where $a$ exhibits a well-defined nonhysteretic peak near $T_{FM}$, which is attributed to the ferromagnetic transition, as well as a broad hysteretic peak in the vicinity of $T_p$, (i.e., $\approx 91$ K on cooling and $\approx 107$ K on warming). The fact that the hysteretic peak at $T_p$, which is associated with much larger lattice parameter changes, is smaller than the peak at $T_{FM}$, reflects a gradual change of the phase fractions in the mixed-phase region. This interpretation is in agreement with the $S$ observed, which shows an extremely broad transition from the insulatorlike one somewhere below $T_{FM}$ to the metallic one below 80 K (Fig. 2). It should be noted that the noticeable anomaly of $\alpha$ as well as the appearance of a new phase in NPD around $T_p$ suggest that the $\rho$ peak may be associated with a change in the bulk property instead of grain boundaries. To verify, the temperature-dependent ceramic-sample striction ($L/L_0$) is plotted in Fig. 5 for both PBMO and PSMO samples. The $L/L_0$ of PBMO, including a distinct kink at $T_{FM}$ and only smaller broad bumps near $T_p$ (although they can be noticed clearly in the $\alpha = d \ln L/dT$ of Fig. 2) agrees nicely with the phase-weighted unit-cell volume determined from the NPD data, and that of PSMO exhibits only one kink at $T_{FM}$. While $L/L_0$ is nearly identical for these two materials in the “mostly I4/mcm” region of PSMO below 80 K, the transformation around $T_p$ in PSMO is accompanied by a significant volume increase, when viewed in comparison to that of PSMO in the FMM state. Above the ferromagnetic transition temperatures, the two curves are nearly coincident once again. The transition around $T_p$ seems to be associated with a phase transition related the change of the cell volume.

The widely separated values of $T_{FM}$ and $T_p$ are unusual compared to most low-$\sigma^2$ manganites, such as PSMO, which undergoes a simultaneous PM-to-FM and metal-insulator transition at $T_{FM} \approx 263$ K (Figs. 1 and 5). The well correlations among the NPD, $S$, $L/L_0$, and $\rho$ data here, however, suggests that the Ibmm phase of PBMO might be FMI above $T_p$. The natural of this intermediate FMI state in PBMO can be better understood by comparing the cell volumes of
PBMO and PSMO (Figs. 4 and 5). The insulating $Ibmm$ PBMO cells above $T_p$ appear to be larger than that expected from the FMM cells of PSMO. It has been proposed and later confirmed that the cell volume of manganites is mainly determined by the nature of the Mn-O bonds.\cite{21} In particular, the bonds associated with SE interactions are typically longer than those of DE interactions. Such an increase of cell volumes at the FMM-FMI transition has been previously reported in La$_{0.88}$Sr$_{0.12}$MnO$_3$ and La$_{0.875}$Sr$_{0.125}$MnO$_3$,\cite{11,20} where it was attributed to the difference in the relative strengths of the DE and SE interactions; the FMM state being dominated by DE interactions and the FMI state being dominated by competing SE interactions. We, therefore, tentatively attribute the intermediate FMI state in PBMO to similar competitions between SE and DE. The local lattice distortions in high-$\sigma^2$ manganites significantly suppress the DE interaction through their lower carrier mobility, which shows up as both the 80 K suppression of $T_{FM}$ and the tenfold increase of the resistivity above $T_M$ from PSMO to PBMO (Fig. 1). The contributions of SE, hence, may become dominated in an intermediate temperature range until the increase of the carrier mobility with further cooling which allows the DE to dominate again. In such a scenario, the phase separation observed over a broad $T$ range will also be rather natural based on the possible mesoscale inhomogeneity of the lattice distortion.

Terashita et al. recently explained the FMI state in the (La$_{1-x}$Gd$_x$)$_{0.7}$Ca$_{0.3}$MnO$_3$ system in terms of Gd- and La-rich clusters with distinct electronic and magnetic properties.\cite{7} The Gd-rich regions would still be in the insulating FM state between $T_{FM}$ and $T_p$, and break the percolating paths. In such a scenario, $|S|$ should decrease through $T_{FM}$, and $M_{FC}$ increase through $T_p$ (as additional parts of the sample enter the FM state) on cooling. Because the opposite behavior is observed in the present study of PBMO, the FMI state of PBMO appears to be more consistent with the SE-dominated FMI state of La$_{0.875}$Sr$_{0.125}$MnO$_3$. The cell volumes in the two cases is certainly consistent with the interpretation.

The $M_{FC}$ of the PBMO and PSMO in a low field of 500 G is compared in the inset of Fig. 5. For the PSMO sample, the $M_{FC}$ in the FMM state plateaus below $T_{FM}$ and remains virtually constant as the temperature decreases. For the PBMO sample, the $M_{FC}$ also plateaus just below $T_{FM}$. Below 100 K, however, the $M_{FC}$ starts to decrease toward a significantly lower plateau. The difference in $M_{FC}$ between the two plateaus is almost 10%. It diminishes with the increase of H and disappears above 1.0 T (Fig. 1). The trend is again consistent with the $M_{FC}$ observed in La$_{0.875}$Sr$_{0.125}$MnO$_3$.

IV. CONCLUSION

A distinguishable FMI state exists in Pr$_{0.7}$Ba$_{0.3}$MnO$_3$ between $T_{FM} \approx 180$ K and $T_p \approx 120$ K. The structural changes at the ferromagnetic transition are minor, whereas the ferromagnetic-insulating phase with $Ibmm$ symmetry transforms incompletely to a low-temperature ferromagnetic metal with $I4/mcm$ symmetry over a broad range of temperatures below $T_p$. Magnetization, resistance, and thermopower measurements suggest that the FMI state of Pr$_{0.7}$Ba$_{0.3}$MnO$_3$ is similar to the FMI state of La$_{1-x}$Sr$_x$MnO$_3$ (0.1 $\leq x \leq$ 0.14), which occurs due to an unusual dominance of ferromagnetic superexchange interactions. An enhanced tendency toward electron localization due to lattice disorder in cation-size-mismatched perovskites may weaken the influence of the DE interaction, and offers a natural interpretation of the FMI state. Comparisons with Pr$_{0.7}$Sr$_{0.3}$MnO$_3$, which has a small A-site cation-size mismatch and no intermediate FMI state, support these conclusions.

ACKNOWLEDGMENTS

The authors thank D. K. Ross for electron microprobe measurements, J. Kulik for TEM data, and Simine Short for assistance with NPD data collection. This work is supported in part by NSF Grant, the T. L. L. Temple Foundation, the John and Rebecca Moores Endowment, and the State of Texas through TCSUH, and at LBNL by DOE. Research at ANL was supported by the U.S. Department of Energy, Office of Science under Contract No. W-31-109-ENG-38.
19 Z. Jirak, private communication.