Optical evidence of mixed-phase behavior in manganite films

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(Rceived 25 September 2008; published 17 December 2008)

Synchrotron infrared measurements were conducted on a self-doped La_{0.8}MnO_{3−δ} (x ~0.8) film. From these measurements we determined the conductivity and the temperature dependence of the effective number of carriers. While the metal-insulator transition temperature (T_MI) and the magnetic ordering temperature (T_C) approximately coincide, the onset of the change in the free carrier density occurs at a significantly lower temperature (~45 K below). This suggests that local distortions exist below T_MI and T_C which trap the ε_sp conduction electrons. These regions with local distortions constitute an insulating phase which persists for temperatures significantly below T_MI and T_C.

DOI: 10.1103/PhysRevB.78.220404

PACS number(s): 75.47.Lx, 78.20.Ls, 64.75.St, 72.80.—r

R_{1−x}A_xMnO_3 (R: trivalent rare-earth ions; A: divalent alkaline-earth ions) has been widely studied due to the colossal magnetoresistance (CMR) observed. 1–6 Divalent cation doping induces a change from Mn^{3+} to Mn^{4+}. The induced holes in the ε_sp level create a mixed-valence system. These materials have also attracted much theoretical and fundamental physics interest since they exhibit intimate coupling of spin, lattice, orbital, and charge degrees of freedom. This coupling results in a ground-state energy landscape with multiple minima corresponding to different charge, spin, and structural configurations. Small external perturbations (such as temperature, pressure, substrate strain, magnetic fields, and electric fields) can shift the system from one state to another. A mixed valence on Mn sites can also be induced in the La-deficient La_{1−x}MnO_{3−δ} (x > 0, δ > 0) manganite. Both ferromagnetic order and metallic conductivity can be obtained, 7–9 and the transition temperatures can be adjusted by both the oxygen content and the La deficiency. 10,11 One of the open questions about these colossal magnetoresistive oxides concerns the transition of the system from the high-temperature paramagnetic insulating phase (with Jahn-Teller distortion of the MnO_6 polyhedra which trap the conduction-band electrons) to the low-temperature conductive ferromagnetic phase. 12,13 It is thought that just above the metal to insulator transition, regions of metallic phase (Jahn-Teller free) begin to grow within the insulating host and then dominate at low temperature based on structural and optical-mode measurements. 14,15 The nature of this mixed-phase behavior is still under discussion.

Optical experiments are a good way to study the phonon modes and electron-phonon coupling in oxides. 16 In addition, information on the free-carrier concentration can be derived. In previous work, it was found that the onset of the increase in the carrier numbers occurs concomitantly with the peak in resistivity and the onset of the ordered magnetic state. 17–20 In this work, we report on a synchrotron infrared spectroscopic study on self-doped La_{0.8}MnO_{3−δ} (x ~0.8) films. While the metal-insulator transition temperature (T_MI) and the magnetic ordering temperature (T_C) approximately coincide, the change in free-carrier density onset at a significantly lower temperature (~45 K below). This indicates the presence of an insulating phase significantly below the magnetic ordering temperature.

La_{0.8}MnO_{3−δ} films were epitaxially grown on (001) LaAlO_3 (LAO) substrates by liquid injection metal organic chemical vapor deposition. 10 Here we report the results for a ~120-nm-thick film which were also found in a ~410 nm film. The in situ postdeposition annealing leads to the strain relaxation, and it is revealed by x-ray diffraction measurement. 29 The film resistivity is 4.6 × 10^{-4} Ω cm (10 K) acquired by a four-point probe setup, which is comparable with 2 × 10^{-4} Ω cm (5 K) for La_{0.8}CaMnO_3 (x =0.33) films on a LAO substrate 30. The metal-insulator phase-transition temperature (T_MI ~298 K) and the Curie temperature (T_C ~295 K) are quite close (see Fig. 3) and a high magnetization saturation of 3.66 μ_B/Mn (5 K) is achieved under a 0.2 T magnetic field. We have defined T_MI and T_C to be onset parameters corresponding to the peak in resistivity 31 and the onset of the magnetization, respectively.

Synchrotron reflectivity spectra were measured at the U2A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. This beamline has a Bruker IFS 66/s vacuum spectrometer equipped with a Bruker IKScope-II microscope, a mercury cadmium telluride detector, and a KB beam splitter for mid-IR; a custom made infrared microscope with long working distant (40 mm) reflecting objective; a 3.5 micron mylar beamsplitter; and a Si bolometer detector for far-IR. The infrared frequency range covers 100–8000 cm^{-1} with a spectral resolution of 4 cm^{-1}. A ~0.5-μm-thick gold layer was deposited on the film as a reflective reference mirror. The sample was mounted on the cold finger of a continuous flow cryostat, and the measurement temperatures were 304 (beginning), 282, 275, 265, 255, 245, 225, 200, 150, 125, 100, 80, 50, 20, and 10 K, which included the metal-insulator transition region.

The reflectivity spectra for the film and the bare substrate are given in Figs. 1(a) and 1(b), respectively. The vertical dashed lines correspond to phonon modes seen in other manganites. 32,33 Note the systematic enhancement of the reflectivity with decreasing temperature. Small spectral variations in the insulating LAO substrate at different temperatures can be seen in Fig. 1(b). In Fig. 1(a) the spectra (304, 282, and 275 K) show prominent LAO-like resonances in the frequency range 100–550 cm^{-1} and small differences are found in the region above 550 cm^{-1}.

More detailed information can be obtained from the re-
The optical conductivity $[\sigma(\omega)]$ can be obtained from the dielectric function: \(\sigma(\omega) = \frac{\varepsilon_\infty - \varepsilon(\omega)}{i\omega}\). Temperature-dependent $\sigma(\omega)$ are plotted for the film [Fig. 2(b)] and the substrate [Fig. 2(c)]. The spectral weight of the Drude components of the film increases as the temperature decreases and the peak above 1000 cm$^{-1}$ which like a small polaron feature moves toward the low-frequency side with decreasing temperature (as has been discussed in detail in Refs. 34 and 39). The peak maximum shifts from $\sim 5100$ cm$^{-1}$ at 304 K to $\sim 4300$ cm$^{-1}$ at 282 K. The polaron shifts to the low-energy side quickly and below 255 K the spectral weight increases dramatically as the carrier mobility increases with reduced temperature. Below 200 K, the reflectivity spectra and the optical spectra vary slowly with the temperature. Figure 2(c) shows LAO substrate optical spectra at two different temperatures. The positions do not change significantly with temperature (<4 cm$^{-1}$) while the amplitudes vary.

In addition, the zero-frequency conductivity, plasma frequency ($\omega_p$), and resistivity are related by $\sigma(0) = \frac{\omega_p^2}{4\varepsilon_\infty}$, $\omega_p^2 = \frac{4\varepsilon_\infty}{m^*\rho}$, and $\rho = \frac{1}{4\varepsilon_\infty\omega_p^2}$. We plotted the dc resistivity and calculated resistivity [from $\sigma(0)$] in Fig. 3(a) with the magnetization. The resistivity data sets have a consistent trend and...
show good agreement for temperatures where the sample is more metallic, indicating that the D-L model is appropriate. Figure 3(a) inset shows that the deficient La$_{0.8}$MnO$_{3-x}$ is a normal CMR material in terms of the widths of the transition regions (for magnetization and resistivity) compared with La$_{2/3}$Ca$_{1/3}$MnO$_3$ film. Note the similarity in widths in the magnetization and resistivity transition regions.

The effective carrier number density $N_{\text{eff}}(T, \omega_c)$ is proportional to the integrated optical conductivity spectral weight: $N_{\text{eff}}(T, \omega_c) = \frac{1}{\pi \omega_c} \int \left| \text{Re} \sigma(\omega) \right|^2 d\omega$. We use a cutoff frequency ($\omega_c$) of 5000 cm$^{-1}$ to calculate the number density ($N_{\text{eff}}$). $N_{\text{eff}}(T)$ and Drude weight (DW) (the $N_{\text{eff}}$ of free carriers only) are plotted in Fig. 3(b) (see Ref. 20). By examining the cutoff frequency dependence of the shape of $N_{\text{eff}}$ vs temperature in the broad set of manganite data in Refs. 35 and 40, we found that the onset profile is independent of $\omega_c$ for cutoff frequencies ranging from 4800 to 32 000 cm$^{-1}$. Moreover the onset temperature found is insensitive to the choice of $\epsilon_{\infty}$ over a physically meaningful range. It can be seen that the onset of the increase in $N_{\text{eff}}$ (~253 K) is significantly below $T_{\text{MI}}$ and $T_C$. The free-carrier Drude weight is small compared with the $N_{\text{eff}}$ and its onset occurs at ~245 K. The results indicate that the increase in carrier concentration lags the onset of magnetic order by ~45 K.

The results suggest a more complex mechanism for the transition to the low-temperature phase in manganites. It is consistent with the existence of regions with significant local distortions below $T_{\text{MI}}$ and $T_C$ which trap the $\epsilon_{\infty}$ conduction electrons. These regions with local distortions constitute an insulating phase which persists for temperatures significantly below $T_{\text{MI}}$ and $T_C$. Low spin scattering will lead to the observed initial large resistivity drop as a result of magnetic ordering of the $t_{2g}$ spins enabling Mn-Mn site hopping when reducing temperature below $T_C$. Further reductions in resistivity are then due to reductions in the volume of the minority insulating phase which then increases the number of free carriers. The origin of the flattening of the reflectivity spectra at low temperature is due to the increased number of minority insulating phase which then increases the number of free carriers. These regions with local distortions constitute an insulating phase which persists for temperatures significantly below $T_{\text{MI}}$ and $T_C$.

In conclusion, we have explored the temperature-dependent infrared reflectivity spectra of La$_{0.8}$MnO$_{3-x}$/LAO....

TABLE I. D-L model fitting parameters at 304, 282, 275, 265, 150, 125, and 10 K. Note: $\omega_c$, $\omega_p$, and $\Gamma$ in unit cm$^{-1}$.

| $\omega_c$ | 5.2 | 5.6 | 5.5 | 5.5 | 5.5 | 5.5 | 5.5 |
| $\omega_p$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $\Gamma_0$ | 1016 | 1184 | 1508 | 6413 | 6782 | 8142 |
| $\Gamma_0$ | 17 | 98 | 314 | 531 | 442 | 366 |
| $\omega_{1/2}$ | 167 | 162 | 167 | 168 | 173 | 175 | 185 |
| $\omega_{1/2}$ | 1039 | 925 | 826 | 718 | 760 | 950 | 769 |
| $\Gamma_1$ | 34 | 33 | 18 | 18 | 23 | 13 | 21 |
| $\omega_{1/2}$ | 356 | 350 | 350 | 350 | 378 | 381 | 382 |
| $\omega_{1/2}$ | 1500 | 1515 | 1455 | 1319 | 2489 | 2941 | 3271 |
| $\Gamma_2$ | 107 | 112 | 100 | 90 | 134 | 128 | 169 |
| $\omega_{1/2}$ | 523 | 524 | 524 | 523 | 523 | 535 |
| $\omega_{1/2}$ | 311 | 316 | 383 | 601 | 726 |
| $\Gamma_3$ | 60 | 57 | 72 | 123 | 69 |
| $\omega_{1/2}$ | 584 | 585 | 585 | 586 | 585 | 577 | 575 |
| $\omega_{1/2}$ | 853 | 897 | 885 | 888 | 1010 | 1509 | 1742 |
| $\Gamma_4$ | 53 | 54 | 52 | 52 | 52 | 86 | 97 |
| $\omega_{1/2}$ | 636 | 642 | 641 | 638 | 659 | 656 | 657 |
| $\omega_{1/2}$ | 615 | 533 | 534 | 448 | 877 | 842 | 893 |
| $\Gamma_5$ | 77 | 46 | 48 | 39 | 39 | 30 | 29 |
| $\omega_{1/2}$ | 908 | 958 | 940 | 984 | 1029 | 4226 |
| $\omega_{1/2}$ | 710 | 826 | 861 | 1029 | 4226 |
| $\Gamma_6$ | 328 | 400 | 413 | 540 | 702 |
| $\omega_{1/2}$ | 4881 | 4177 | 4304 | 4129 | 2123 | 1732 | 1899 |
| $\omega_{1/2}$ | 8541 | 15085 | 15952 | 17064 | 17908 | 14955 | 19233 |
| $\Gamma_7$ | 2215 | 3526 | 3822 | 4181 | 3682 | 3037 | 1988 |
| $\omega_{1/2}$ | 5564 | 8988 | 9178 | 7795 | 2654 | 2318 |
| $\omega_{1/2}$ | 19684 | 17922 | 17315 | 6794 | 13366 | 15866 |
| $\Gamma_8$ | 7416 | 9101 | 8447 | 2729 | 1763 | 1474 |
ordering temperature ($T_{\text{cut}}$) and the magnetic ordering temperature ($T_{\text{c}}$) approximately coincide, the free-carrier density onset occurs at a significantly lowered temperature (~45 K below). The conductivity was found to be systematically enhanced at lower temperatures. These results are consistent with the existence of insulating regions at temperatures significantly below the metal-insulator and magnetic ordering temperatures.

This research was funded by NSF (Grants No. DMR-0512196 and No. INT-0233316) and CNRS/NSF (Project No. 14550). U2A beamline is supported by COMPRES, the Consortium for Materials Properties Research in Earth Sciences under NSF Cooperative Agreement No. EAR01-35554 and U.S. Department of Energy (DOE-BES and NNSA/CDA). Use of the National Synchrotron Light Source, Brookhaven National Laboratory was supported by the Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

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