PHYSICAL REVIEW B, VOLUME 63, 132404

Competition of charge, orbital, and ferromagnetic correlations in layered manganites

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(Received 5 December 2000; published 7 March 2001)

The competition of charge, orbital, and ferromagnetic interactions in layered manganites is investigated by magneto-Raman scattering spectroscopy. We find that the colossal magnetoresistance effect in the layered compounds results from the interplay of orbital and ferromagnetic double exchange correlations. Inelastic scattering by charge-order fluctuations dominates the quasiparticle dynamics in the ferromagnetic-metal state. It is suppressed at low frequencies, consistent with the opening of a charge-density wave pseudogap.

DOI: 10.1103/PhysRevB.63.132404 PACS number(s): 75.30.Vn, 71.10.Hf, 71.30.+h, 78.30.−j

Quantum criticality, driven by competing electronic ground states, can lead to dramatic tunability of the physical properties of strongly correlated condensed-matter systems.[1,2] A current case of great interest is the role of collective excitations in the phenomenon of ''colossal'' magnetoresistance (CMR) in manganites. These excitations represent the various interactions of electrons in the Mn d orbitals.[3] Charge ordering (CO), where the $\mathrm{Mn}^{3+}/\mathrm{Mn}^{4+}$ ions form an ordered sublattice, occurs because the large on-site Coulomb repulsion forbids the double occupancy of the e_g orbitals. Ordering of the Mn^{3+} e_g orbitals (OO) results from a cooperative Jahn-Teller (JT) distortion. Antiferromagnetism is associated with the superexchange coupling of the t_{2g} electron spins. The ferromagnetic-metal (FM) ground state is attributed to Mn^{3+}—O—Mn^{4+} double exchange, a consequence of strong Hund's coupling which favors hopping between Mn atoms with parallel spin. The CMR effect is observed in ferromagnetic metals as a large decrease in their electrical resistance near the Curie temperature (T_C) upon application of a magnetic field (H).[4] There is a growing realization that the interplay of these collective excitations is responsible for the sensitivity of this phenomenon to external perturbations.[5]

A preponderance of evidence points to the coexistence of different electronic phases in pseudocubic manganites. Thermopower measurements have shown that the entropy for $T \gg T_C$ is smaller than that of an uncorrelated insulator.[6] This agrees with a diffuse x-ray scattering study[7] that finds the JT polarons in the paramagnetic state are correlated. The observation of $\mathrm{Mn}^{3+}/\mathrm{Mn}^{4+}$ striped phases[8] suggests that the correlation is related to CO and OO. Charge-ordered compounds exhibit a transition to the FM phase above an H that is small compared to their CO transition temperature (T_{co}), i.e., $g\mu_B H \ll k_B T_{co}$,[9] indicating that a small free energy separates these ground states. This could lead to CO persisting with the FM double exchange correlations below T_C. Earlier infrared studies[10,11] indicated such coexistence. They estimate the itinerant carrier effective mass as $m^*/m_e \approx 13$ (Ref. 10) or 80 (Ref. 11), anomalously much larger than the specific-heat value of $m^* \approx 2.5 m_e$ (Ref. 12). Within the CO scenario, the difference can be reconciled by a charge-density wave opening a partial gap at the Fermi level (E_F) below T_C, suppressing both the Drude spectral weight and the density of states at E_F. Consequently, the optical mass increases while the specific-heat mass decreases. However, a recent work[13] has shown that the Drude weights were significantly underestimated in the bulk optical studies.[10,11] Measurements on thin films of optimally doped compounds yielded $m^*/m_e \approx 3–4$, comparable to the specific-heat mass.[13] This result rules out the presence of strong CO correlations in the FM state of the pseudocubic compounds.[13]

In this work, we investigate the competition of the collective ground-state excitations in the layered manganites which should be more pronounced in these two-dimensional (2D) systems since the propensity towards a quantum critical point is exacerbated in lower dimensions.[1,2] Indeed, the CMR effect is enhanced in the quasi-2D manganites.[14] We demonstrate that the CMR phenomenon in these compounds results from the interplay of OO and FM double exchange correlations. In contrast with the pseudocubic materials, we find evidence in the layered manganites for an unusual quasiparticle dynamics in the FM state arising from strong inelastic scattering by charge-order fluctuations.

We investigate single crystals of the double layer manganites $R_{2-2x}\mathrm{Sr}_{1+2x}\mathrm{Mn}_2\mathrm{O}_7$ with cations $R=\mathrm{La}$ or Nd and doping $x=0.4$ or 0.5. These crystals consist of MnO_2 bilayers separated by insulating $(R,\mathrm{Sr})_2\mathrm{O}_2$ sheets, a quasi-2D structure responsible for their anisotropic transport and magnetic properties.[14,15] $\mathrm{LaSr}_2\mathrm{Mn}_2\mathrm{O}_7$ is an antiferromagnetic insulator which undergoes CO and OO below $T_{co} \simeq 210$ K.[16]

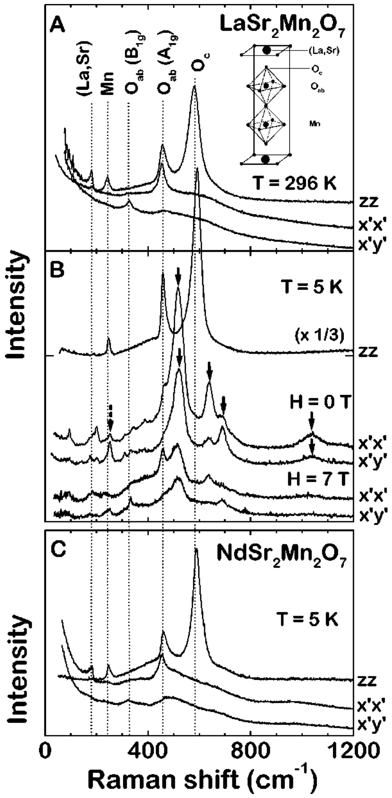

FIG. 1. (A) For $T>T_{co}$, only the phonons of the tetragonal crystal structure of $LaSr_2Mn_2O_7$ are observed. (B) For $T<T_{co}$, new modes in $x'x'$ and $x'y'$ are activated by the charge (dashed arrow) and orbital (solid arrow) ordering within the MnO_2 plane. Magnetic field quenches these modes. (C) The new modes are absent in $NdSr_2Mn_2O_7$.

Electron diffraction[16] provides evidence for real-space checkerboard pattern of Mn^{3+} and Mn^{4+} ions and coherent JT displacement of the O atoms within the MnO_2 planes. In $NdSr_2Mn_2O_7$, this ordered state is suppressed by the La to Nd substitution which results in a chemical pressure that relaxes the in-plane JT distortions.[17] $La_{1.2}Sr_{1.8}Mn_2O_7$ is a CMR compound with $T_C \simeq 120$ K.[14] Raman spectroscopy was conducted for temperatures $T=5-350$ K and magnetic fields $H=0-7.5$ T in a backscattering geometry using a triple-grating spectrometer with a liquid-nitrogen-cooled charge-coupled device detector and the 514.5-nm Ar^+ laser line as excitation. Charge and orbital correlations are probed via the optical phonons activated by the lowered symmetry due to the ordering within the MnO_2 layers. For the double layer manganites, the following scattering geometries extract the dominant A_{1g} and B_{1g} normal modes of the D_{4h} point group: $zz \Rightarrow A_{1g}$, $x'x' \Rightarrow A_{1g}+B_{2g}$, $x'y' \Rightarrow B_{1g}+A_{2g}$ where the notation $\hat{\mathbf{e}}_i \hat{\mathbf{e}}_s$ refers to the polarization of the incident and scattered light and z is parallel to the c axis while x' and y' are along the Mn—O bonds in the MnO_2 plane. Quasiparticle dynamics is inferred from electronic Raman scattering.

For $T>T_{co}$, $LaSr_2Mn_2O_7$ reveals only the $4A_{1g}+B_{1g}+5E_g$ phonons associated with the tetragonal crystal structure $[I4/mmm\ (D_{4h}^{17})]$ of double layer manganites discussed in earlier works.[18,19] Figure 1(A) shows the A_{1g} modes at 185, 246, 460, and 576 cm^{-1} in $x'x'$ and zz and the B_{1g} mode at 325 cm^{-1} in $x'y'$ for $T=296$ K, labeled by their corresponding c-axis atomic vibrations.[18] We note that our assignment of the 246 cm^{-1} peak as a Mn phonon disagrees with that of Yamamoto *et al.*[19] which attributed this peak to another (La,Sr) vibration. The absence of a corresponding feature in the single-layer $La_{1/2}Sr_{3/2}MnO_4$ (Ref. 19) supports our assignment since this phonon is not Raman active because Mn occupies a site of inversion symmetry.

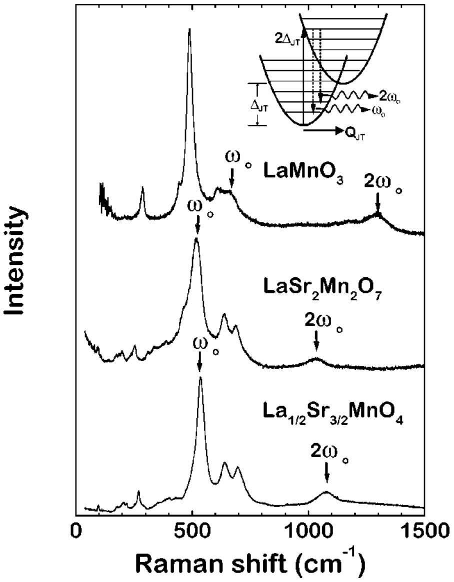

FIG. 2. Franck-Condon effect in manganites with orbital-ordered ground state.

For $T<T_{co}$, new peaks emerge in the $x'x'$ and $x'y'$ but not in the zz spectra of $LaSr_2Mn_2O_7$. These are marked by the arrows in Fig. 1(B) for $T=5$ K. In Fig. 1(C), these features are absent in $NdSr_2Mn_2O_7$ in which the ordering is quenched by the La to Nd cation substitution. In Fig. 2, as seen by Yamamoto *et al.*[19] as well, the same peaks are observed in the ground state of $La_{1/2}Sr_{3/2}MnO_4$. These results demonstrate that the new modes are activated by CO and OO within the MnO_2 plane in layered manganites.

In contrast to our results in Fig. 1(B), Yamamoto *et al.*[19] report the suppression of the new modes in $LaSr_2Mn_2O_7$ as T is lowered to 10 K that they attribute to a transition from the charge-ordered state to a type-A layered antiferromagnet. Similar re-entrant behavior is reported by others.[20] Our observation of the new peaks at $T=5$ K is not due to laser heating since we used a smaller power (~ 5 mW) to take the spectra in Fig. 1(B) compared to the one reported in Ref. 19. Furthermore, the T dependence of our $LaSr_2Mn_2O_7$ spectra is very similar to that of Yamamoto *et al.*'s[19] for $T \gtrsim 100$ K and in which we find the onset to activate these peaks close to T_{co}. With laser heating this onset should shift to a lower T. We account for the discrepancy between the two results at low T to the difference in the compound's composition. As shown below and in Ref. 21, the lower doped $La_{1.2}Sr_{1.8}Mn_2O_7$ displays a similar quenching of the new peaks at low T. Such similarity implies that the doping of $LaSr_2Mn_2O_7$ studied in Ref. 19 is below $x=0.5$.

The peak at 250 cm^{-1} in $x'y'$ (dashed arrow) in Fig. 1(B) is a CO activated Mn phonon. Above T_{co}, the uniform Mn charge distribution in the $\mathrm{Mn}^{3.5+}$—O_{ab}—$\mathrm{Mn}^{3.5+}$ bonds precludes observing this mode. Below T_{co}, the ordered Mn^{3+}—O_{ab}—Mn^{4+} sublattice breaks this symmetry leading to the observed Raman activity. The anomalous B_{1g} character of this new Mn mode reflects the twofold symmetric checkerboard $\mathrm{Mn}^{3+}/\mathrm{Mn}^{4+}$ pattern in the CO state.

The remaining new modes (solid arrows) in Fig. 1(B) are the OO activated O_{ab} phonons. Yamamoto *et al.*[19] assigned the peaks at 520 and 636 cm^{-1} in $x'x'$ and at 522 and 694 cm^{-1} in $x'y'$ to breathing and JT O_{ab} phonons of the lattice with coherent JT distortions. We present in Fig. 2 the evidence that the distortion is due to e_g orbital ordering. Weak overtones at twice the frequency of the JT phonons are seen in the OO ground state of pseudocubic $\mathrm{LaMnO_3}$, double layer $\mathrm{LaSr_2Mn_2O_7}$, and single layer $\mathrm{La_{1/2}Sr_{3/2}MnO_4}$. Multiphonon scattering due to anharmonicities is ruled out since the two-phonon peaks do not correlate with the strongest phonons observed in these compounds [for instance, the $2\omega_o$ peak is absent in the zz spectrum of $\mathrm{LaSr_2Mn_2O_7}$ in Fig. 1(B) and it does not correspond to the strong peak at 495 cm^{-1} in $\mathrm{LaMnO_3}$ in Fig. 2]. Figure 2 inset depicts a resonance Raman mechanism adapted from Ref. 22. The lower parabola represents the OO ground-state configuration while the upper parabola is the lowest lying excited state of a self-trap exciton (Δ_{JT}) that results from an orbital flip followed by the relaxation of the surrounding O_{ab} atoms. The self-localized nature of these electronic states leads to Franck-Condon vibrational sidebands. An electron excited by an incident photon with $\hbar\omega = 2\Delta_{JT}$ can relax to the various ground-state vibrational levels accounting for the multiphonon features in our Raman spectra. The relative intensity, $I(2\omega_o)/I(\omega_o)$, of the Franck-Condon peaks is smaller in $\mathrm{La_{1/2}Sr_{3/2}MnO_4}$ and $\mathrm{LaSr_2Mn_2O_7}$ ($\simeq 1/8$) than in $\mathrm{LaMnO_3}$ ($\simeq 1/2$). This is explained as follows. In $\mathrm{LaMnO_3}$, with only Mn^{3+} ions, the electron-phonon interaction is effective in localizing the e_g electron[22] because hopping is suppressed by the large on-site Coulomb repulsion. The presence of Mn^{4+} sites in the half filled layered manganites increases hopping resulting in the diminished $2\omega_o$ peak.

Previous transport and magnetization studies[9] have indicated that the charge-order ground state is unstable in the presence of FM correlations. This is directly demonstrated in Fig. 1(B) which shows the quenching of the CO and OO peaks in $\mathrm{LaSr_2Mn_2O_7}$ when $H = 7$ T is applied. Earlier Raman works[18,21] in the CMR compound $\mathrm{La_{1.2}Sr_{1.8}Mn_2O_7}$ have also shown the melting of the CO and OO sublattice in the FM ground state. Based on similarities with the layered $x = 0.5$ compounds, Yamamoto *et al.*[21] have argued the persistence of the CO and OO peaks in $\mathrm{La_{1.2}Sr_{1.8}Mn_2O_7}$ and demonstrated their disappearance below T_C. In our earlier work,[18] we reported the suppression of the CO activated Mn phonon in the FM state.[23] Below, we elucidate the dynamics of this melting.

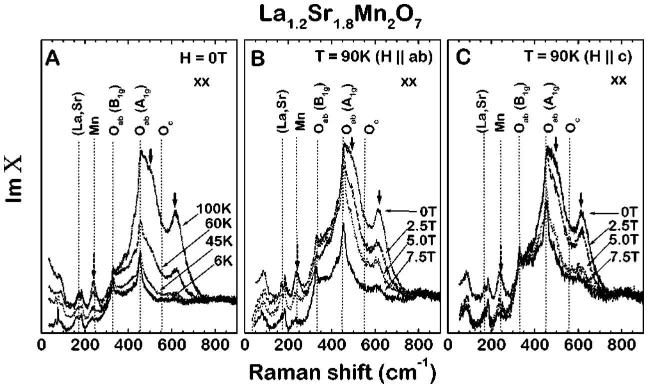

FIG. 3. Persistence of charge (dashed arrow) and orbital (solid arrow) correlations in $\mathrm{La_{1.2}Sr_{1.8}Mn_2O_7}$ and their melting by lowering the temperature (A) or raising the magnetic field (B) and (C). An electronic background continuum below T_C is suppressed at low frequencies.

In $\mathrm{La_{1.2}Sr_{1.8}Mn_2O_7}$, the CO induced Mn phonon is at 240 cm^{-1} while the OO activated O_{ab} peaks are at 514 and 623 cm^{-1} as shown in the xx ($\Rightarrow A_{1g} + B_{1g}$) spectra in Fig. 3. These peaks are progressively quenched either by lowering T below T_C [Fig. 3(A)] or by raising H [Figs. 3(B) and (C)], proof that the melting is driven by the ferromagnetic alignment of the Mn spins. As illustrated in Fig. 4(A), CO sets in near $T \simeq 270$ K and grows with decreasing T peaking below T_C at $T \simeq 100$ K for $H = 0$ T. In contrast, Fig. 4(B) shows that OO exists in the entire paramagnetic-insulating state attaining a maximum just above T_C at $T \simeq 130$ K. With $H = 7.5$ T, both correlations drop precipituously near T_C. The T and H behaviors of OO are similar to that of the short-range polaron correlations manifested in the diffuse

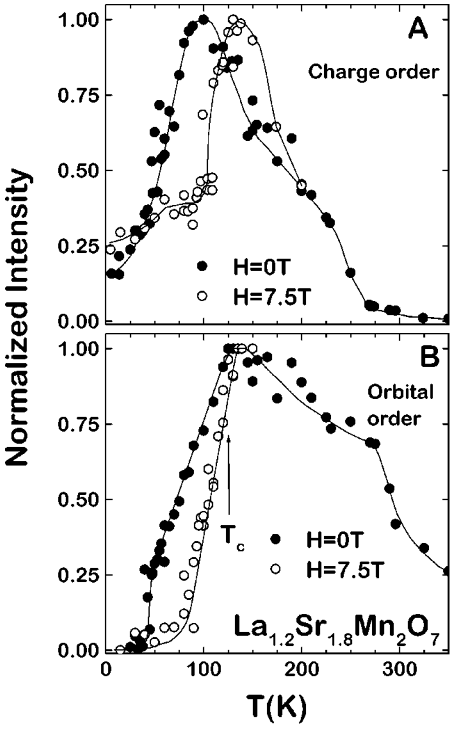

FIG. 4. Temperature and magnetic field dependence of the normalized intensity of the (A) CO activated Mn and (B) OO induced O_{ab} phonons in $\mathrm{La_{1.2}Sr_{1.8}Mn_2O_7}$.

x-ray and neutron scattering in $La_{1.2}Sr_{1.8}Mn_2O_7$.[24] On the other hand, the presence of the Mn peak below T_C seen in Fig. 4(A) indicates that CO correlations persist against the ferromagnetic instability. An additional support for this conjecture is our observation in Fig. 3 of an electronic Raman continuum below T_C.

Electronic Raman scattering from CMR manganites has been observed recently.[21,25] The spectra are characterized by diffusive scattering above T_C that is suppressed in the FM ground state. We observed such behavior in $La_{1.2}Sr_{1.8}Mn_2O_7$, similar to that observed by Yamamoto *et al.*[21] Here, we emphasize an unusual suppression of the electronic continuum below T_C that is not reported in Ref. 21. This is shown in Fig. 3 which plots the Raman response function $\mathrm{Im}\,\chi(\omega,T)$, depicting our measured Raman scattering intensity $I(\omega,T)$ upon correction by the Bose-Einstein thermal factor.[21,25] Just below T_C, $\mathrm{Im}\,\chi(\omega,T)$ is seen as a nearly flat background continuum. For $T \ll T_C$ [Fig. 3(A)] or upon raising H at $T \lesssim T_C$ [Figs. 3(B) and (C)], $\mathrm{Im}\,\chi(\omega,T)$ is suppressed below $\omega \simeq 300\ \mathrm{cm}^{-1}$. While the pseudocubic manganites manifest a similar featureless $\mathrm{Im}\,\chi(\omega,T)$ in the FM state, such low-frequency suppression is not observed.[25] This difference is attributed to an effect of the lower dimensionality in the layered compounds. It signals a strong inelastic scattering by persistent CO fluctuations that develop into a collective charge-density wave excitation well below T_C. This picture is also suggested by other studies. Optical conductivity[26] betrays a small Drude contribution implying an optical mass that is much larger than that derived by a specific-heat study.[27] These are indicative of a charge-density wave pseudogap opening at E_F, in accord with the severe depression of the quasiparticle states at E_F revealed by an angle-resolved photoemission study[28] and suggested by the re-entrant insulating state below $T \simeq 50$ K invariably seen in transport measurements.[14,27] It is interesting to note that the latter temperature is comparable to the onset frequency where $\mathrm{Im}\,\chi(\omega,T)$ is suppressed.

In conclusion, the correspondence between the OO dynamics and the paramagnetic-insulator to ferromagnetic-metal transition in $La_{1.2}Sr_{1.8}Mn_2O_7$ is evidence that competing orbital and ferromagnetic double exchange interactions around T_C is responsible for the CMR phenomenon in manganites. Our observation of an unusual quasiparticle dynamics below T_C in $La_{1.2}Sr_{1.8}Mn_2O_7$ is reminiscent of the unconventional behavior of the normal state of high-temperature superconducting cuprates,[2] suggesting that the FM ground state in the layered manganites is another example of a non-Fermi liquid.

We acknowledge A. J. Millis for elucidating the importance of charge ordering in the CMR manganites and P. B. Allen for pointing out the Franck-Condon model of the orbital excitations. We thank Dr. R. V. Datla of NIST-Optical Technology for his support of this work. J.F.M. acknowledges the U.S. DOE, Office of Basic Energy Sciences-Materials Sciences Division, under Contract No. W-31-109-ENG-38.

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