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

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Abstract

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 the orbital and ferromagnetic double-exchange correlations. Inelastic scattering by charge-order fluctuations dominates the quasiparticle dynamics in the ferromagnetic-metal state. The scattering is suppressed at low frequencies, consistent with the opening of a charge-density wave pseudogap.

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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 involving the electrons in the Mn \(d\) orbitals [3]. Charge ordering (CO), where the Mn\(^{3+}\)/Mn\(^{4+}\) ions form an ordered sublattice, occurs because the large on-site Coulomb repulsion forbids the double-occupancy of the \(e_g\) orbitals. Orbital ordering (OO) of the Mn\(^{3+}\) \(e_g\) electron orbitals results from a cooperative Jahn-Teller (JT) distortion induced by electron-phonon interactions. 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 in which parallel spin alignment favors electron hopping between neighboring Mn atoms. 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 the different electronic phases in the 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 recent x-ray diffuse scattering study [7] that finds the JT polarons in the paramagnetic state are correlated. The observation of Mn\(^{3+}/\)Mn\(^{4+}\) striped phases [8] suggests that the correlation is related to charge and orbital ordering. Charge-order insulator compounds exhibit a transition to the FM phase above an \(H\) that is small compared to the charge ordering transition temperature \((T_{co})\) i.e., \(g\mu_B H \ll k_B T_{co}\) [9], indicating a small free energy separates these two ground states. This could lead to charge ordering persisting with the ferromagnetic double-exchange correlations below \(T_C\). Evidence for such coexistence was reported in earlier infrared studies [10,11] which estimate the itinerant carrier effective mass as \(m^*/m_e \approx 13\) [10] or 80 [11]. These are anomalously much larger than \(m^* \approx 2.5m_e\), the
value from specific heat \[12\]. Within the charge ordering 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 charge-order 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. The effects of competing ground states 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 orbital and ferromagnetic 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.

Our investigation was carried out on single-crystals of the double-layer manganites \(R_{2-2x}Sr_{1+2x}Mn_2O_7\) with the cations \(R = \text{La or Nd}\) and for doping \(x = 0.4\) or \(0.5\). These crystals consist of \(\text{MnO}_2\) bilayers separated by insulating \((R, \text{Sr})_2\text{O}_2\) sheets, a quasi-2D structure responsible for their anisotropic transport and magnetic properties \[14,15\]. \(\text{LaSr}_2\text{Mn}_2\text{O}_7\) is an antiferromagnetic insulator which undergoes charge and orbital ordering below \(T_{co} \approx 210\) K \[16\]. Electron diffraction \[16\] provides evidence for real-space checkerboard pattern of \(\text{Mn}^{3+}\) and \(\text{Mn}^{4+}\) ions and coherent JT displacement of the O atoms within the \(\text{MnO}_2\) planes. In \(\text{NdSr}_2\text{Mn}_2\text{O}_7\), this ordered state is suppressed because the substitution of La by the larger Nd cation results in a chemical pressure that relaxes the in-plane JT distortions \[17\]. \(\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\) exhibits CMR behavior near \(T_C \approx 120\) K \[14\] associated with the paramagnetic-insulator to ferromagnetic-metal transition. Raman spectroscopy was con-
ducted over the temperatures $T = 5$ K to 350 K and magnetic-fields $H = 0$ T to 7.5 T in a back-scattering geometry using a triple-grating spectrometer with a liquid-nitrogen cooled CCD 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. Polarized Raman scattering was used to identify the phonon symmetries. For the double-layer manganites, the following scattering geometries extract the dominant $A_{1g}$ and $B_{1g}$ 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 $\hat{e}_i\hat{e}_s$ 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.

In the uniform state ($T > T_{co}$), shown in Fig. 1A for $T = 296$ K, LaSr$_2$Mn$_2$O$_7$ reveals only the phonons of its tetragonal crystal structure. This structure has $I4/mmm$ ($D_{4h}^{17}$) symmetry for which we expect $4A_{1g} + B_{1g} + 5E_g$ Raman-active normal modes. As predicted, there are four peaks at 180 cm$^{-1}$, 250 cm$^{-1}$, 460 cm$^{-1}$ and 570 cm$^{-1}$ in the $x'x'$ and $zz$ spectra corresponding to the $A_{1g}$ modes and one at 325 cm$^{-1}$ in the $x'y'$ for the only allowed $B_{1g}$ mode. To determine the dominant atomic vibration in these modes, we invoke the four-fold and two-fold rotational symmetry of the $A_{1g}$ and $B_{1g}$ modes, respectively. The four-fold axially symmetric $c$-axis vibrations of the (La,Sr), Mn, and apical O$_c$ atoms along the tetragonal axis are respectively assigned to the three $A_{1g}$ phonons at 180 cm$^{-1}$, 250 cm$^{-1}$, and 570 cm$^{-1}$. The in-plane O$_{ab}$ atoms have two Raman-active vibrations along the $c$-axis, a four-fold symmetric in-phase motion attributed to the remaining $A_{1g}$ mode at 460 cm$^{-1}$ and a two-fold symmetric out-of-phase motion comprising the $B_{1g}$ phonon at 325 cm$^{-1}$.

In the charge-ordered state ($T < T_{co}$), new peaks marked by the arrows in Fig. 1B for $T = 5$ K emerge in the $x'x'$ and $x'y'$ spectra but not in $zz$. Fig. 1C highlights the absence of these features in NdSr$_2$Mn$_2$O$_7$ in which the ordering is quenched by the La to Nd cation substitution. From these results, we conclude that the new modes are activated by the lowered symmetry within the MnO$_2$ layers in LaSr$_2$Mn$_2$O$_7$.

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

The remaining new modes (solid arrows) in Fig. 1B are the phononic signatures of orbital ordering. The concomitant cooperative JT distortion of such ordering induces the peaks at 520 cm$^{-1}$ and 636 cm$^{-1}$ in $x'x'$ and at 522 cm$^{-1}$ and 694 cm$^{-1}$ in $x'y'$. Recently, Yamamoto et al. \cite{18} assigned these modes to breathing and JT vibrations of the O$_{ab}$ atoms. The evidence for $e_g$ orbital ordering is presented in Fig. 2. It is suggested by the appearance of weak overtones at twice the frequency of the JT phonons in the OO ground state of pseudocubic LaMnO$_3$, double-layer LaSr$_2$Mn$_2$O$_7$ and single-layer 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 LaSr$_2$Mn$_2$O$_7$ in Fig. 1B and it does not correspond to the strong peak at 495 cm$^{-1}$ in LaMnO$_3$ in Fig. 2). Fig. 2 inset depicts a resonance Raman mechanism adapted from the recent work of Allen and Perebeinos \cite{19} on LaMnO$_3$. The lower parabola represents the OO ground state configuration while the upper parabola is the lowest lying excited state of a self-trap exciton ($\Delta_{JT}$) that results from an orbital flip followed by lattice relaxation via a JT distortion ($Q_{JT}$) of the 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 La$_{1/2}$Sr$_{3/2}$MnO$_4$ and LaSr$_2$Mn$_2$O$_7$ ($\simeq 1/8$) than in LaMnO$_3$ ($\simeq 1/2$). This is explained by noting that in LaMnO$_3$, with only Mn$^{3+}$ ions, the large on-site Coulomb repulsion suppresses hopping making the electron-phonon interaction effective in self-trapping the $e_g$ electron \cite{19}. This condition is alleviated in the half-filled layered manganites due to the presence of Mn$^{4+}$ sites.
resulting in the reduced $2\omega_o$ peak.

In previous works, the magnetic field-induced melting of the charge-order ground state was infered only indirectly from the observation of an antiferromagnetic-insulator to ferromagnetic-metal transition in transport and magnetization studies [9]. Direct structural evidence for this effect is given in Fig. 1B showing the suppression of the CO and OO features in LaSr$_2$Mn$_2$O$_7$ when $H = 7$ T is applied. Further insight into the origin of the suppression is gained from our findings in the CMR compound La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$.

The phononic signatures of the charge-ordered state are also observed in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$. In the $xx$ ($\Rightarrow A_{1g} + B_{1g}$) spectra in Fig. 3, the CO induced Mn peak is at 240 cm$^{-1}$ while the OO activated O$_{ab}$ phonons are at 514 cm$^{-1}$ and 623 cm$^{-1}$. These peaks are progressively quenched either by lowering $T$ below $T_C$ (Fig. 3A) or by raising $H$ (Figs. 3B and C), proof that the melting of the charge-order ground state is driven by the ferromagnetic alignment of the Mn spins. The dynamics of the competition of charge, orbital, and ferromagnetic correlations in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ is illustrated in Fig. 4. In Fig. 4A, charge ordering sets in near $T \simeq 270$ K and grows on lowering $T$ peaking below $T_C$ at $T \simeq 100$ K for $H = 0$ T. In contrast, Fig. 4B shows that orbital coherence 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 charge and orbital correlations drop precipitously near $T_C$. The $T$ and $H$ behaviors of the orbital correlations are similar to that of the short-range polaron correlations manifested in the diffuse x-ray and neutron scattering in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ [20]. The correspondence between these behaviors and the paramagnetic-insulator to ferromagnetic-metal transition in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ is evidence that competing orbital and ferromagnetic double-exchange interactions around $T_C$ is responsible for the CMR phenomenon in manganites. On the other hand, the presence of the Mn peak below $T_C$ seen in Fig. 4A indicates that charge 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 can arise from charge-density fluctuations. This is expressed in terms of an electronic polarizability, $\chi(\omega, T)$, which is obtained from the Raman scattering
intensity $I(\omega, T)$ using the relation $I(\omega, T) \propto \text{Im} \chi(\omega, T)/[1 - \exp(-\hbar \omega/k_B T)]$. Fig. 3 shows typical $\text{Im} \chi(\omega, T)$ derived from our measured spectra. Just below $T_C$, $\text{Im} \chi(\omega, T)$ is seen as a nearly flat background continuum. For $T \ll T_C$ (Fig. 3A) or upon raising $H$ at $T \lesssim T_C$ (Fig. 3B and C), $\text{Im} \chi(\omega, T)$ is suppressed below $\omega \simeq 300$ cm$^{-1}$. While the pseudocubic manganites manifest a similar featureless $\text{Im} \chi(\omega, T)$ in the FM state, the low-frequency suppression is not observed [21]. 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 below $T_C$. This picture is also suggested by other studies. Optical conductivity [22] betrays a small Drude contribution implying an optical mass that is much larger than that derived by a specific heat study [23]. 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 [24] and suggested by the re-entrant insulating state below $T \simeq 50$ K invariably seen in transport measurements [14] [23]. It is interesting to note that the latter temperature is comparable to the onset frequency where $\text{Im} \chi(\omega, T)$ is suppressed.

In conclusion, competing collective groundstate excitations is a ubiquitous phenomenon in the manganites whose understanding is crucial in unraveling the wide tunability of their physical properties. Our observation of an unusual quasiparticle dynamics below $T_C$ in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ 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.

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FIGURES

FIG. 1. A. For $T > T_{co}$, only the phonons of the tetragonal crystal structure of LaSr$_2$Mn$_2$O$_7$ 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$_2$Mn$_2$O$_7$.

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

FIG. 3. Persistence of charge (dashed arrow) and orbital (solid arrow) correlations in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ 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.

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 La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$. 
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Figure 2 ("Competition of charge, orbital....." by D.B. Romero etal.)
Figure 3 ("Competition of charge, orbital...." by D.B. Romero etal.)
Figure 4 ("Competition of charge, orbital..." by D.B. Romero et al.)