Orbital dynamics: The origin of the anomalous optical spectra in ferromagnetic manganites

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(June 30, 1998)

We discuss the role of orbital degeneracy in the transport properties of perovskite manganites, focusing in particular on the optical conductivity in the metallic ferromagnetic phase at low temperatures. Orbital degeneracy and strong correlations are described by an orbital t-J model which we treat in a slave-boson approach. Employing the memory-function formalism we calculate the optical conductivity, which is found to exhibit a broad incoherent component extending up to bare bandwidth accompanied by a strong suppression of the Drude weight. Further, we calculate the constant of T-linear specific heat. Our results are in overall agreement with experiment and suggest low-energy orbital fluctuations as the origin of the strongly correlated nature of the metallic phase of manganites.

PACS number(s): 72.80.Ga, 71.27.+a, 71.30.+h, 72.10.-d

Perovskite manganese oxides, $R_{1-x}A_x$MnO$_3$ (where $R$ and $A$ represent rare-earth and divalent metal ions, respectively) exhibit rich physical behavior, whose origin lies in the mutual interplay between spin, charge, orbital, and lattice degrees of freedom as well as in the strong correlations among electrons. The key elements of electronic structure are the Mn 3d orbitals, which due to crystal-field splitting and strong Hund coupling are in a $(t_2_g)^3(e_g)^1$ configuration for $x=0$, with holes being induced in the twofold degenerate $e_g$ orbitals for $x>0$. Electrons in the $t_2_g$ and $e_g$ orbitals are usually considered as localized and itinerant, respectively.

Early work on the transport properties of manganites has focused primarily on the double-exchange scenario, which also, competing with antiferromagnetism, results in a complex magnetic phase diagram. The renewed interest in manganese oxides sparked by the recent discovery of a very large magneto-resistance has led to a controversial discussion of the role of lattice and orbital degrees of freedom: the effect of onsite correlations among $e_g$ electrons, however, has mostly been discarded. On the experimental side, these correlations seem to be strong even in the metallic state of manganites, despite the fact that double exchange strongly suppresses the spin dynamics below $T_c$. This can be deduced, e.g., from the observation of only a small discontinuity at the Fermi level in photoemission spectra. Particularly striking in this respect are recent measurements of the optical conductivity of La$_{1-x}$Sr$_x$MnO$_3$. The conductivity in the metallic state was found to consist of two components: (1) a narrow Drude peak at $\omega < 0.02$ eV with strongly suppressed weight and (2) a broad incoherent part extending up to $\omega \approx 1$ eV. It is remarkable that the incoherent component remains finite even at $T \ll T_c$ where ferromagnetic moments have completely saturated, clearly indicating the presence of other degrees of freedom besides spin fluctuations. The fact that the incoherent part of the spectrum extends to rather high frequencies suggests these degrees of freedom to be of electronic origin, possibly resulting from the orbital degeneracy of $e_g$ orbitals as has been proposed by several authors.

Shiba, Shina, and Takahashi ascribe the excitations leading to the incoherent structure of the optical conductivity to transitions between two fermionic bands within the degenerate $e_g$ orbitals, which they find to result in a spectrum extending up to fermionic bandwidth. While their model indicates the role of orbital degeneracy, it neglects the $e_g$-electron correlations. A more elaborate treatment of both, orbital degeneracy and electron correlations, was done by Ishihara, Yamanaka, and Nagaosa. Starting from an orbital-charge separation scheme these authors showed that orbital fluctuations are strong enough to prevent orbital ordering from developing. Performing numerical calculations based on a phenomenological model that simulates orbital disorder by static randomness in the hopping matrix elements they further were able to recover the characteristic features of the optical conductivity spectrum, though no Drude component was obtained.

In this paper we report on the first microscopic theory of the optical conductivity which combines strong correlations and orbital degeneracy. The transport properties of manganites are shown to be highly incoherent even in the ferromagnetic phase due to strong scattering of charge carriers on dynamical orbital fluctuations. This gives rise to a broad optical absorption spectrum extending up to bare bandwidth accompanied by a strong suppression of the Drude weight. The theory further accounts for the small values of specific heat found experimentally.

Assuming complete ferromagnetic saturation of electronic spins, which will henceforth be neglected, our starting point is an orbital t-J model:

\[
H = - \sum_{\langle ij \rangle_{\gamma}} \sum_{\alpha\beta} \left( t^{\alpha\beta}_{ij} c^\dagger_{i\alpha} \hat{c}_{j\beta} + \text{H.c.} \right) + J \sum_{\langle ij \rangle_{\gamma}} \left( \tau^\gamma_i \tau^\gamma_j - \frac{1}{4} n_in_j \right),
\]

where $\langle ij \rangle_{\gamma}$ indicates summation over manganese
nearest-neighbor bonds in spatial direction \( \gamma \in \{ \hat{x}, \hat{y}, \hat{z} \} \).

The operator \( \hat{c}_{i\alpha}^\dagger = e_{i\alpha}^\dagger (1 - n_i) \) creates an electron at an empty site \( i \) with orbital pseudospin \( \alpha \) for which we use the notation \( \uparrow = d_{3z^2-r^2} \) and \( \downarrow = d_{x^2-y^2} \). The anisotropic transfer matrix elements are given by

\[
t_{z/y}^{\sigma\beta} = t \begin{pmatrix} 1/4 & \mp \sqrt{3}/4 \\ \mp \sqrt{3}/4 & 3/4 \end{pmatrix}, \quad t_{z}^{\sigma\beta} = t \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix},
\]

allowing for interorbit transitions in the \( xy \) plane. The strength of the pseudospin interaction is controlled by the superexchange coupling constant \( J = 2t^2/U \), where \( U \) is the onsite repulsion between spin-parallel \( e_g \) electrons. Since \( U \) is believed to be large we assume \( J < t \). The pseudospin operators of Eq. (1) are defined as

\[
\tau^x/y = \frac{1}{4} \left( \sigma^z \pm \sqrt{3}\sigma^x \right), \quad \tau^z = \frac{1}{2} \sigma^z,
\]

with Pauli matrices \( \sigma^x \) and \( \sigma^z \). We note that in the real system Jahn-Teller coupling further contributes to the \( J \) term of Hamiltonian (1). Three-site hopping terms that are contained in a general orbital \( t-J \) model are neglected for simplicity.

We calculate the optical conductivity \( \sigma(\omega) \) using the memory-function formalism. While not rigorous this method yields exactly the leading terms of a high-frequency expansion of \( \sigma(\omega) \) and is believed to give reasonably accurate results over the whole frequency range if no critical low-energy modes as in one-dimensional systems exist. Within this framework the optical conductivity \( \sigma(\omega) \) is expressed via the memory function \( M(\omega) \)

\[
\sigma(\omega) = \chi_0 \frac{i}{\omega + M(\omega)}.
\]

where \( \chi_0 \) is the zero-frequency current-current correlation function. The memory function is given by

\[
M(\omega) = -\frac{1}{\omega \chi_0} \left[ f(\omega) - f(0) \right],
\]

with \( f(\omega) \) being the correlation function of force operators \( F_x = [J_z, H] \). The transport properties of the system are isotropic in the orbital-disordered phase, allowing us to select the current along the \( z \) direction which is of the simple form

\[
J_z = -\frac{i e t}{N a^3} \sum_{(ij)z} \left( \hat{c}_{i\uparrow}^\dagger \hat{c}_{j\uparrow} - \text{H.c.} \right),
\]

where \( N \) is the number of lattice sites and \( a \) denotes the lattice constant. The force operator consists of two parts \( F_z^t \) and \( F_z^J \) corresponding to the \( t \) and \( J \) term of Hamiltonian (1). Due to the relative smallness of the coupling constant \( J \) as compared to \( t \) the latter term is expected to contribute only little to the optical conductivity and will therefore be neglected. For the former term one finds

\[
F_z^t = -\frac{i e t^2}{2 N a^3} \sum_{i,\gamma,\delta} \sum_{\alpha\beta} \left( R_{i+\delta} - R_i \right) t_{\gamma\beta} \times \left( B_{i\alpha} \hat{c}_{i+\delta}^\dagger \hat{c}_{i+\gamma,\beta} + \text{H.c.} \right),
\]

with the bosonic operator

\[
B_{i\alpha} = (2 - n_i + \sigma_z^\alpha) \delta_{\alpha\uparrow} + (\sigma_i^\downarrow - i \sigma_i^\uparrow) \delta_{\alpha\downarrow},
\]

where double occupancy of sites is excluded.

We employ a slave-boson theory to express Hamiltonian (1) and the force operator, Eq. (5), in terms of fermionic spinon operators \( f_{i\alpha} \) and bosonic holon operators \( h_i \). The pseudoparticles fulfill the local constraint

\[
f_{i\uparrow}^\dagger f_{i\uparrow} + f_{i\downarrow}^\dagger f_{i\downarrow} + h_i^\dagger h_i = 1 \quad \text{which is relaxed to a global one.}
\]

On a mean-field level, the dynamics of spinons and holons are given by decoupling Hamiltonian (1) into fermionic and bosonic parts, introducing mean-field parameters \( \chi = \langle f_{i\uparrow}^\dagger f_{j\uparrow} \rangle z \) and \( \sqrt{\tau} = \langle h_i \rangle x \), where \( x \) is the concentration of doped holes. The mean-field Hamiltonian describes two fermionic Gutzwiller bands of width \( W_x = 6(\tau x + \chi J) \) and one bosonic band of width \( W_h = 12 \tau \chi \).

From analogy to the conventional \( t-J \) model the slave-boson representation with its fermionic description of low-lying orbital excitations is expected to describe well an orbitally disordered state far from critical instabilities towards orbital ordering. The existence of such an orbital liquid state is strongly supported by the analysis of Ishihara, Yamanaka, and Nagaosa, who find orbital disordered even within a slave-fermion Schwinger-boson representation which favors orbital ordering. Assuming the stability of the disordered state, we select the slave-boson representation, noting, however, that short-range orbital correlations will not be fully captured in this picture.

The memory function, Eq. (2), is calculated via the force-force correlation function, replacing holon operators by their mean-field value and keeping fluctuations around this value up to first order. Diagram (a) of Fig. 1 describes transitions between the two coherent Gutzwiller bands of the spinon mean-field Hamiltonian. These interband transitions are allowed due to the fact that the \( t \) term of Hamiltonian (1) is not diagonal in orbital quantum numbers. Using a free-fermion picture, similar transitions were found by Shiba, Shina, and Takahashi to contribute to the optical conductivity spectrum. The presence of electron correlations, however, strongly suppresses the spectral weight associated with these processes and shifts the upper bound of the corresponding absorption spectrum to low energies.

Diagrams (b) and (c) of Fig. 1 purely originate from correlations among electrons and are absent in a free theory. They describe transitions between a coherent Gutzwiller and a highly-incoherent band with corresponding contributions to the optical conductivity spectrum that extend approximately up to bare fermionic bandwidth. We note that such broad incoherent absorption was also found in a recent finite-temperature
diagonalization study performed on small clusters. Diagram (b) accounts for the composite nature of charge carriers in a strongly correlated system reflected by the spinon-holon convolution. The force operator employed in the calculation of this diagram yields terms involving two as well as three lattice sites. The two-site terms are already contained in the current operator and thus also appear in a direct calculation of the optical conductivity via the current-current correlation function. The three-site terms, however, are intrinsic to the force-force correlation function and partially account for vertex corrections. Diagram (c) finally describes scattering of carriers on pseudospin fluctuations. We note that the force term $F^0$ neglected before contains only terms involving three lattice sites of small amplitude, supporting our previous approximation to discard this term.

The spinon and holon propagators of Fig. 1 are calculated with the self-energy corrections shown in Fig. 2. The spinon self-energy diagrams (a) and (b) describe scattering on pseudospin and holon-density fluctuations, respectively. The quasiparticle weight, which is proportional to $x$ on the mean-field level, is further suppressed by these incoherent scattering processes. This smallness of quasiparticle weight is consistent with the experimental observation of only a small discontinuity in the spectral-weight function at the Fermi energy as seen in photoemission spectra. The bosonic self-energy diagrams (c) and (d) describe scattering on fluctuations of the spinon bond-order parameter, creating a broad incoherent peak in the bosonic spectral function.

The expressions obtained from the diagrams in Figs. 1 and 2 contain several integrations over momentum space which we solve numerically using a Monte Carlo algorithm. The zero-frequency current-current correlation function $\chi_0$ of Eqs. 3 and 4 is obtained from the spinon mean-field Hamiltonian as $\chi_0 = 2x\chi t e^2/a$. We choose a hole-doping concentration of $x = 17.5\%$ and set $J = 0.4t$. The value of the spinon bond-order parameter is numerically determined to be $\alpha = 0.25$, the lattice constant is set to $a = 3.9$ Å. The real part of the optical conductivity, Eq. 5, consists of the Drude component $\sigma_D(\omega) = \pi e^2 \sum_i \delta(\omega - \epsilon_i)$ and the regular part $\sigma_{\text{reg}}(\omega)$. The spectrum of the regular part is shown in Fig. 2 indicated by a solid line. We compare our theoretical result to experimental data obtained by Okimoto et al. for 17.5% doped La$_{1-x}$Sr$_x$MnO$_3$ at $T = 9$ K represented by the dashed line in Fig. 2. The only free parameter which we use to fit the theoretical to the experimental curve is the free fermionic bandwidth which we fix by setting $\epsilon_F = 0.36$ eV consistent with band structure calculations.

Good agreement between experiment and theory is found for intermediate and high frequencies. We stress that no additional fitting parameter is needed to obtain the correct absolute values of $\sigma_{\text{reg}}(\omega)$. The total spectral weight consisting of the Drude part $\sigma_D(\omega)$ and the incoherent part $\sigma_{\text{reg}}(\omega)$ is in agreement with experiment as can be seen from the effective charge-carrier concentration defined as

$$N_{\text{eff}} = \frac{2m_0 a^2}{\pi e^2} \int_0^\infty d\omega (\sigma_D(\omega) + \sigma_{\text{reg}}(\omega)).$$

In the low-frequency region the theoretical curve deviates from the experimental one as a pseudogap opens in the spectrum. As a result our theory does not completely account for the weight transferred to the incoherent part of the spectrum as is reflected by the ratio of total spectral weight to Drude weight; here we obtain a value of 2.8 which compares to $\approx 5$ found experimentally.

The discrepancy between theory and experiment in the low-frequency part of the optical absorption spectrum indicates an additional scattering mechanism to be active at low energies which is not incorporated in our theory. We speculate this mechanism to stem from the closeness of the real system to orbital ordering underestimated in the above slave-boson treatment. Scattering on low-lying orbital collective modes induced by electronic superexchange and Jahn-Teller coupling as well as scattering on phonons will enhance the low-energy region of the spectrum, thus filling the pseudogap. To make the latter point more explicit we calculate the conductivity including electron-phonon effects. Coupling of $e_g$ pseudospins to double-degenerate Jahn-Teller phonons and of charge to the lattice breathing mode are described by

$$H_{\text{JT}} = -\lambda_{\text{JT}} \sum_i \left( (a_i^+ + a_i)\sigma_i^z + i(a_i^+ - a_i)\sigma_i^x \right),$$

$$H_{\text{ch}} = -\lambda_{\text{ch}} \sum_i \left( b_i^+ b_i - n_i \right),$$

respectively. For simplicity, phonons are considered to have dispersionless energy, which we set to $\omega_0 = 0.05$ eV. Corrections to the force-force correlation function and to
the fermionic self-energies are evaluated within a weak-coupling scheme, assuming the dimensionless coupling constant $\zeta = \lambda^2 N(\epsilon_F)/\omega_0$, where $N(\epsilon_F)$ is the total $e_g$-density of states at the Fermi level, to be small below $T_c$. The result, which for $\zeta_{\text{RT}} = \zeta_{\text{ch}} = 0.3$ is shown by the dot-dashed line in Fig. 3, suggests that (possibly strong) lattice effects are present even in the metallic ferromagnetic phase.

We further calculate the constant of $T$-linear specific heat $\gamma$ from the spinon mean-field Hamiltonian. For $x = 17.5\%$ we find $\gamma = 7.2$ mJ/mol K$^2$ as compared to experimental values 5 - 6 mJ/mol K$^2$ (Ref. [5]) and 3.3 mJ/mol K$^2$ (Ref. [6]). Experimentally $\gamma$ was observed to be nearly independent of $x$. In our theory we find $\gamma \propto N^0(\epsilon_F)/(\pi t + \chi J)$; since the bare density of states $N^0(\epsilon)$ exhibits a pseudogap centered around the chemical potential at half-filling, $\gamma$ is rather insensitive to changes in $x$ for moderate hole-doping concentrations; for $x = 30\%$ we in fact find $\gamma = 7.1$ mJ/mol K$^2$.

In summary, we have calculated the optical absorption spectrum of ferromagnetic manganites, emphasizing the role of low-energy orbital fluctuations leading to the strongly correlated nature of the metallic state. The theory explains the large incoherent component of the optical conductivity accompanied by a strong suppression of Drude weight observed experimentally and is also consistent with measurements of the specific heat. The fact that the anomalous transport properties in the ferromagnetic phase are described well supports the orbital-liquid idea and suggests that the orbital degrees of freedom coupled to the lattice are of relevance in the metal-insulator crossover driven by the magnetic transition in manganites. This transition, which due to the double-exchange mechanism is accompanied by a reduction of the mobility of charge carriers, suppresses the energy scale ($\propto x t$) of orbital fluctuations and enhances the Jahn-Teller coupling of these fluctuations to the lattice. Apparently, the picture of an orbital liquid which is quantum disordered by the metallic motion of holes is no longer valid above $T_c$; a disorder-order crossover in the orbital sector is in fact indirectly indicated by the temperature dependence of local lattice distortions experimentally observed. We speculate this crossover to control the metal-insulator transition by further reducing the mobility of charge carriers, thus playing an essential role in enabling the formation of small lattice polarons and their localization above $T_c$.

We wish to thank P. Fulde and P. Horsch for valuable discussions.

FIG. 3. Incoherent part of the optical conductivity $\sigma_{\text{reg}}(\omega)$ as a function of photon frequency $\omega$. The solid line represents the theoretical curve for $x = 17.5\%$, which is fitted to experimental data (dashed line) obtained by Okimoto et al. for La$_{1-x}$Sr$_x$MnO$_3$ at $T = 9$ K. The dot-dashed line corresponds to the theory including lattice effects.

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