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Metal-insulator transition in manganites: Changes in optical conductivity up to 22 eV

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The electronic response of doped manganites at the transition from the paramagnetic insulating to the ferromagnetic metallic state in $La_{1-x}Ca_xMnO_3$ for $x=0.3$ and 0.2 was investigated by dc conductivity, ellipsometry, and vacuum ultraviolet reflectance for energies between 0 and 22 eV. A stabilized Kramers-Kronig transformation yields the optical conductivity and reveals changes in the optical spectral weight up to 22 eV at the metal-to-insulator transition. In the observed energy range, the spectral weight is conserved within 0.3%. The redistribution of spectral weight in this surprisingly broad energy range has important ramifications for the effective low-energy physics. We discuss the importance of the charge-transfer, Coulomb on-site, Jahn-Teller, and long-range Coulomb screening effects to the electronic structure.

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Among strongly correlated materials, the manganites exhibit a wealth of novel properties. For example, some hexagonal insulating materials exhibit multiferroic behavior and the cubic doped manganites show charge ordering and the colossal magnetoresistance (CMR) effect.[1,2] It is clear that the two key ingredients responsible for these diverse phenomena are, first, the high geometrical and spin frustration and, second, the large number of competing interactions, the most important of which are the electron-electron and electron-phonon interactions.[1,3–9]

There is a deep disagreement as to which of these interactions is the primary driving force behind either the insulating phase of the manganites or the metal-to-insulator transition in the doped manganites. Models describing these phenomena involve double exchange, Jahn-Teller (JT), superexchange, and Coulomb on-site (Hubbard U) interactions that yield effective low-energy Hamiltonians, which predict different types of quasiparticle excitations, such as spin excitations, lattice polarons, spin polarons, or orbitons.[3,4,6–21] However, the effective Hamiltonians used to describe the manganites typically ignore the oxygen p bands and consider only an effective manganese d band. It is also generally assumed that the high-energy degrees of freedom can be neglected by a "down folding" of the large number of bands into a single effective band. This implies that there is no redistribution of electronic states between low-energy and high-energy degrees of freedom. On the other hand, if one considers the importance of local interactions and hybridization in correlated materials, one would expect quite pronounced effects at higher energies that are connected to charge-transfer or Mott-Hubbard physics.[15,22–24] Thus, the important test for the effective low-energy picture is to study whether one finds strong exchanges of spectral weight between low and high energies.

Therefore, it is crucial to test the complex nature of the band structure explicitly. The most direct experiment is to measure the dielectric response of a material as a function of temperature and doping. Unfortunately, experimental measurements of the dielectric response implicitly endorse the assumption of effective low-energy models, since the dielectric response of these materials has, in the past, been typically measured only below 3 eV or lower, while the dielectric response above 3 eV is generally assumed to be insensitive to temperature and doping.[11,13–15,17,25–36]

In this study, we present the experimental evidence of spectral-weight changes, i.e., changes in the integrated optical conductivity, from the paramagnetic insulating phase to the ferromagnetic metal phase of $La_{0.7}Ca_{0.3}MnO_3$ ($x=0.3$) and $La_{0.8}Ca_{0.2}MnO_3$ ($x=0.2$) in an unprecedented energy range of 0–22 eV. This observation does not only challenge the assumptions of effective low-energy models of correlated manganites but also of previous measurements examining the temperature and doping dependence of the low-energy dielectric response. We use a combination of dc-conductivity, spectroscopic ellipsometry, and vacuum ultraviolet (VUV)-reflectivity measurements in order to study the evolution of the optical conductivity across the metal-to-insulator transition. Spectral-weight changes that occur at a phase transformation can reveal the relevant energy scales and the source of the free energy associated with that transformation. The main findings of our study are (i) changes in the optical spectral weight exceed energies up to 22 eV. A significant fraction of the spectral weight of the Drude response stems from energies above 3 eV, presumably from transitions centered at 8 and at 12 eV. (ii) In the spectral range between 0 and 22 eV the spectral weight is conserved within 0.3%. Our results question the general validity of effective low-energy one-band quasiparticle models and demonstrate the importance of local interactions on the electronic structure of the manganites. We argue that screening effects of the Mott-Hubbard U, which originate from the polarizability of the atoms and from the charge transfer between Mn and O, are of crucial importance to understand the spectral-weight changes over a wide energy range across the metal-to-insulator transition.

The experiments were performed on high quality and atomically smooth films, including (i) a 165 nm film of $x=0.3$ and (ii) a 150 nm film of $x=0.2$ on orthorhombic $NdGaO_3$ (110) to minimize substrate related strain effects. The metal-to-insulator transition temperature T_{MI} was about 260 K ($x=0.3$) and 150 K ($x=0.2$), respectively. The films are characterized in detail by transmission electron microscopy, atomic force microscopy, x-ray diffraction,[37] x-ray photoemission,[38] ellipsometry and magneto-optical ellipsometry measurements,[32,39] and x-ray absorption spectroscopy (XAS). The XAS experiment was done at SINS beamline of Singapore Synchrotron Light Source.[40] The XAS result shows that our samples are nearly strain free and exhibit bulklike behavior. Four-point resistance measurements were performed to measure the dc conductivity. Spectroscopic ellipsometry measurements were performed in the spectral range between 0.5 and 5.5 eV using a SE 850 ellipsometer and a UHV cryostat.[41] For reflectance measurements in the high-energy range between 4.5 and 22 eV we have used the superlumi beamline at the DORIS storage ring of Hasylab (DESY).[42] The calibration of the monochromator was done by measuring the luminescence yield of sodium salicylate ($NaC_7H_5O_3$).[42] We outfitted the sample chamber with a gold mesh to measure the incident photon flux after the slit of the monochromator. The measurements at the superlumi beamline were very sensitive to small freeze out effects. We maintained a pressure of about 10^{-9} mbar, the temperature above 125 K, and we employed thermal cycling.

Figures 1(a) and 1(b) show the reflectivity data as obtained by spectroscopic ellipsometry and VUV-reflectance measurements for $x=0.2$ and 0.3, respectively. Ellipsometry is a self-normalizing technique, which makes it free from any ambiguities that are related to the normalization of conventional reflectance results. Ellipsometry measures the real and imaginary parts of the dielectric function. From this we calculate the reflectivity. We have used ellipsometry-derived reflectivity between 4.5 and 5.5 eV to normalize the VUV reflectivity. One can see that large changes at low and high energies are observed for both samples through the metal-to-insulator transition. The strongest changes occur at low energies as well as, surprisingly, at rather high energies between 8 and 12 eV. The strength of the changes increases with increased doping, i.e., the increased number of carriers.

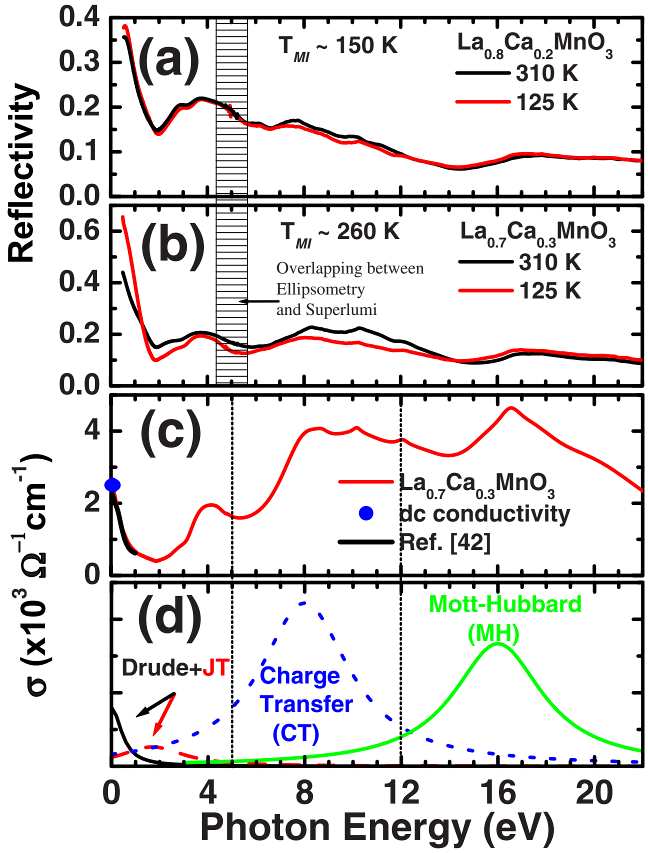

FIG. 1. (Color online) Reflectivity from the self-normalizing ellipsometry setup and the superlumi beamline for temperatures above (black) and below (red/gray) the metal-to-insulator transition for (a) $La_{0.8}Ca_{0.2}MnO_3$ and (b) $La_{0.7}Ca_{0.3}MnO_3$, respectively. (c) Optical conductivity of $La_{0.7}Ca_{0.3}MnO_3$ at 125 K derived from a Kramers-Kronig transformation using dc-conductivity, ellipsometry, and VUV-reflectance data. The black curve reproduces low-energy conductivity of bulk $La_{0.75}Ca_{0.25}MnO_{3-y}$ (Ref. 43). (d) Schematic spectral regions: (i) Drude and Jahn-Teller (0–3 eV), (ii) charge-transfer (3–12 eV), and (iii) local d-d transitions (12–22 eV).

From these reflectivity measurements, it is quite clear that the spectral-weight redistribution associated with the metal-to-insulator transition is not adequately represented by reflectance measurements that are confined to low energies. Further, it is clear from these data that one cannot assume that the high-energy (>3 eV) dielectric response is constant as a function of temperature, and indeed employing such an assumption in a simplified Kramers-Kronig (KK) analysis will likely yield incorrect results for the redistribution of spectral weight across the phase transition.[14,17,29,30,33,34]

In order to reliably obtain the optical conductivity, we have applied the KK transformation to the reflectivity data shown in Figs. 1(a) and 1(b). This procedure yields, as compared to previous studies, much more accurate results due to the application of both the large measured energy window and the use of ellipsometry data. At the high-energy cutoff, we extrapolated our reflectivity by an ω^{-4} power law, while between the 0 eV (i.e., dc limit) and 0.5 eV, we used a linear interpolation. The resulting optical conductivity between 0 and 1 eV matches the dc conductivity at all temperatures and is in excellent agreement with the conductivity of bulk $La_{0.75}Ca_{0.25}MnO_{3-y}$.[43] An example of the optical conductivity up to 22 eV obtained in this way is shown in Fig. 1(c) as representative of the ferromagnetic metallic phase. The basic spectral response of the manganites contains peaks centered around 20, 16, 12, 10, 8, 4, 1 eV, and, in the metallic state, at the dc limit. From Fig. 1(c) we identify three important spectral regions that we display in Fig. 1(d).

Low-energy region—region I. In the low-energy region we identify a strong Drude response and an incoherent background up to about 3 eV. From this incoherent background the pseudogap develops in the insulating state of the manganites. This is the energy range where effective low-energy physics in terms of polarons or the orbital liquid dominates.[7–9] In the undoped material, there is clear evidence that the strong Jahn-Teller effect of the Mn^{3+} is important and results in an orthorhombic lattice distortion that couples, for instance, via an orbital exciton strongly to the electronic structure.[5,6,13] The typical energy scale of these Jahn-Teller related excitations varies between 0.5 and 3 eV. In the low-temperature limit the Jahn-Teller effect vanishes below T_{MI}.[44]

Medium-energy region—region II. The charge-transfer excitations from the bands involving oxygen $2p$ states to the bands involving manganese d states are found above 3 eV.[45] The local charge-transfer energy to move an electron from the O^{2-} ion to the Mn^{3+} ion is essentially given by the difference in the ionization potential of O and the electron affinity of Mn in the actual solid. This involves the free ion values corrected for the very large Madelung potential reduced by the effects of covalency and the screening due to the polarizability of the surroundings. Studies of these effects estimate a charge-transfer energy of 3–8 eV.[15,22,45,46] Furthermore, the crystal-field splitting and the Jahn-Teller effect would split the energies of the charge-transfer excitations. The cubic crystal-field splitting of about 2 eV results into two main charge-transfer bands of 4 and 8 eV. Due to the additional Jahn-Teller splitting of 0.5–1 eV we would expect four different charge-transfer bands: (i) O $2p$ to $Mn(t_{2g}-JT)$; (ii) O $2p$ to $Mn(t_{2g}+JT)$; (iii) O $2p$ to $Mn(e_g-JT)$; and (iv) O $2p$ to $Mn(e_g+JT)$. Thus, we expect transitions at 3.5, 4, 8, and 8.5 eV. Additionally, due to strong orbital overlap of Mn d and O p states, some contribution of screened transitions related to intra-atomic Coulomb interaction within Mn d, U_{dd} and intra-atomic Coulomb interaction within O p, U_{pp} cannot be excluded.[47] On the other hand, O $2p$ to La/Ca d transitions may also occur in this energy range.[34] However, from our doping and temperature dependences, it is hard to explain the large changes in the spectral weight, especially in the medium- and high-energy regions, based on the O $2p$ to La/Ca d transitions only.

High-energy region—region III. The high-energy scale is related to the bare energy of the Mn d to d transitions (unscreened Mott-Hubbard U) between neighboring Mn ions. These are optically allowed. Moreover, there is still a possibility of weak unscreened d-d transitions within the same Mn ion due to disorder in these materials.[13] For electrons that are on one site, i.e., in the same orbital, one would expect such an energy to be of the order of 14.4 eV when calculating the Coulomb energy $e^2/(4\pi\epsilon_0 r)$ with a maximum distance for the two charges of 10^{-10} m, i.e., the size of a Mn ion. This also implies that the on-site interaction is instantaneous on the subfemtosecond time scale. This is in qualitative agreement with Auger spectra on Cu_2O and cluster calculations setting the U_{dd} to about 10 eV.[48] Considering the above mentioned energy scales, one would expect that the transitions are split at 12 and 16 eV by crystal field effects. However, hybridization between Mn d and O p levels would screen these transitions and redistribute the spectral weight of the unscreened 14.4 eV peak down to the medium- and low-energy regions as we have discussed before. In fact, this could establish a strong connection between high, medium, and low energies.[22,49]

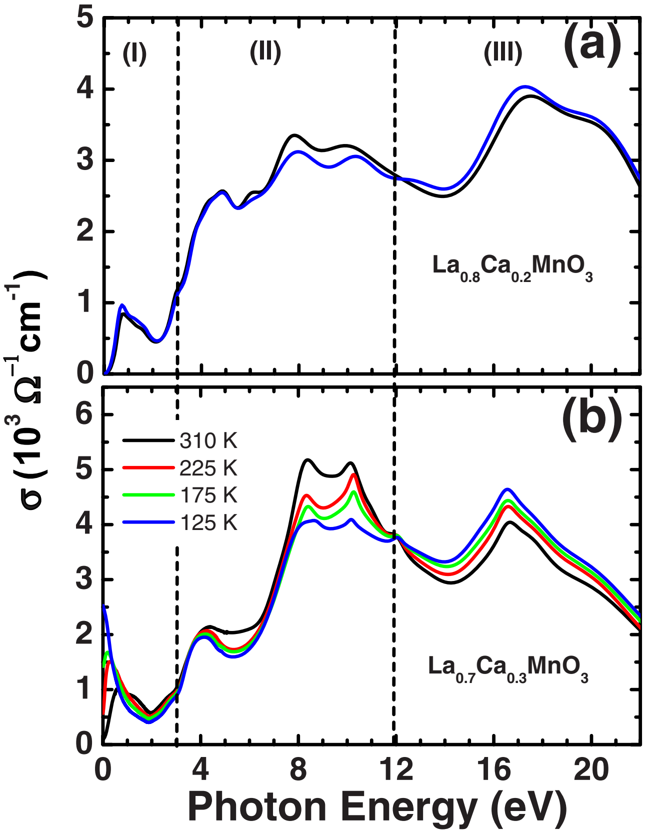

FIG. 2. (Color online) Optical conductivity in $La_{0.8}Ca_{0.2}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ as a function of temperature across the metal-to-insulator transition shown in (a) and (b), respectively. Note the spectral-weight changes at high energies.

Figure 2 shows the optical conductivity through the metal-to-insulator transition for (a) $x=0.2$ and (b) $x=0.3$. In particular, the strongly suppressed Drude response in the optical conductivity for $x=0.2$ at the metal-to-insulator transition is evident, leading to the most pronounced changes at higher energies around 8–12 eV. At 310 K, i.e., above the insulator-to-metal transition, the spectra show clear changes as a function of doping. The screening terms also change at the insulator-to-metal transition and as a function of doping as it can be seen when comparing Figs. 2(a) and 2(b).

In the following, we discuss the temperature dependence of the optical conductivity, which is shown in Fig. 2, as well as the integrated spectral weight shown in Fig. 3. In Figs. 2(a) and 2(b) we find clearly strong renormalization effects

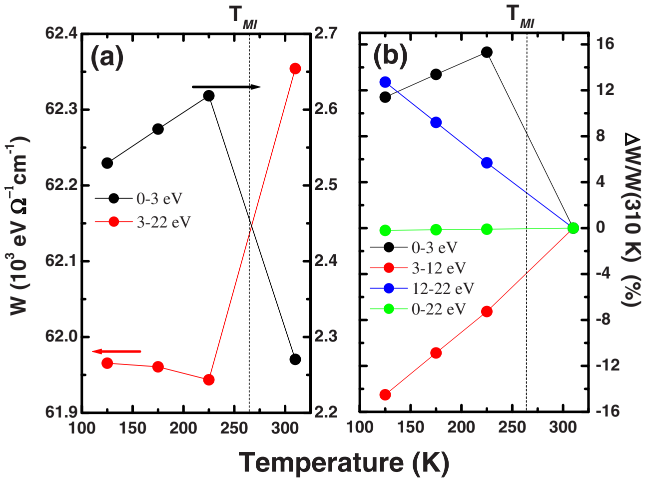

FIG. 3. (Color online) (a) Integrated spectral weight of $La_{0.7}Ca_{0.3}MnO_3$ in different spectral regions. There is a spectral-weight gain in the low-energy region up to 3 eV. (b) Relative spectral-weight changes, $\Delta W(T)/W(310\text{ K})$, in different regions and the overall integrated spectral weight. $\Delta W/W$ is defined as spectral-weight difference $\Delta W = \int_{\omega_1}^{\omega_2} \Delta\sigma(\omega,T)d\omega$ normalized to W (310 K) of the respective energy range. The overall spectral weight is conserved within 3/1000.

as a function of temperature and shifts of spectral weight between the different fundamental processes as outlined in Fig. 1(d). In order to discuss these effects quantitatively we display the spectral-weight changes in the three important energy regions in Figs. 3(a) and 3(b): (i) the low-energy region (0–3 eV), (ii) the medium-energy region (3–12 eV), and (iii) the high-energy region (12–22 eV). Note that the medium- and the high-energy region are separated by an isosbestic point at 12 eV.

It is important to note that (1) the strong temperature dependent occurs at above 4 eV and (2) the exchange of spectral weight within the low-energy region is not sufficient to explain the strength of the spectral weight up to 3 eV in the metallic state, indicating that spectral weight is transferred from much higher energies. We conclude that up to one-third of the spectral weight comes from higher energies, i.e., presumably the charge-transfer or Mott-Hubbard bands above 3 eV. The exchange of spectral weight at high energies between 10 and 22 eV could be related to spin dependent transitions in the ferromagnetic state in connection with a "bare" *d*-*d* transition. For ferromagnetically correlated spins the transition will involve high spin states in the final state of both ions, while for antiferromagnetically correlated spins the transition will involve a low or intermediate spin state on one of the ions in the final state. Hund's rule coupling would cost three times J_H ($\approx$0.8 eV) of about 2.4 eV when comparing transitions to these different *d* states.[31]

Another possible way to explain intuitively the relatively strong spectral redistributions at high, medium, and low energies is the following. Hund's rule coupling leads to spin polarized and spin split bands. Therefore, it can be important in the medium- and high-energy region as well. As an example, take a simple single band half-filled Hubbard model.[50] If the neighboring spins are antiparallel then an interatomic transition is allowed and occurs at an energy U (where U can be much higher than 3 eV). However if the spins are parallel then the transition is not allowed. So a small energy scale of, in this case, an interatomic superexchange can affect the spectral weight at much higher energies well above 3 eV.

Traditionally, the optical features at low energy are related to electric and magnetic properties. However, our results suggest that the electronic band structure at high energy is as important as the low-energy features. In fact, as one can see from the $La_{0.8}Ca_{0.2}MnO_3$ result [Fig. 2(a)], the optical conductivities at medium and high energies change dramatically comparing to the low-energy part across metal-to-insulator transition. This implies the importance of the medium- and high-energy regions to the low-energy regions.

It is also interesting to compare our result with photoemission spectroscopy. Valence band photoemission measurements on $La_{1-x}Sr_xMnO_3$ (Refs. 51 and 52) and $La_{1-x}Ca_xMnO_3$ (Ref. 53) have observed that photoemission spectra are temperature dependent in the energy range even up to 12 eV. In their interpretation, O 2*p* and Mn 3*d*-O 2*p* hybridization states occur in the charge-transfer region as in our interpretation. It is concluded that there is a spectral weight transferred in a broad energy range across the metal-to-insulator transition. However, it is important to note here that photoemission spectroscopy directly probes the occupied state, however it does not reveal the charge conservation.

In conclusion, we have proposed a method to reveal electronic band structure of correlated systems by measuring the optical conductivity in an unprecedented energy range between 0 and 22 eV across the metal-to-insulator transition. By investigating spectral-weight changes exceeding energies of more than 22 eV, we have identified three important spectral regions that we attribute: a Drude and Jahn-Teller, a charge-transfer response, and Coulomb *d*-*d* transitions. Our results put strong constraints on the interpretation of the physics in correlated materials such as the manganites. The effective low-energy physics has to reflect appropriately the higher-energy scales that are involved in the metal-to-insulator transition.

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