Role of Oxygen Electrons in the Metal-Insulator Transition in the Magnetoresistive Oxide La$_{2-x}$Sr$_{1+2x}$Mn$_2$O$_7$ Probed by Compton Scattering

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We have studied the [100]-[110] anisotropy of the Compton profile in the bilayer manganite. Quantitative agreement is found between theory and experiment with respect to the anisotropy in the two metallic phases (i.e. the low temperature ferromagnetic and the colossal magnetoresistant phase under a magnetic field of 7 T). Robust signatures of the metal-insulator transition are identified in the momentum density for the paramagnetic phase above the Curie temperature. We interpret our results as providing direct evidence for the transition from the metallic-like to the adixed ionic-covalent bonding accompanying the magnetic transition. The number of electrons involved in this phase transition is estimated from the area enclosed by the Compton profile anisotropy differences. Our study demonstrates the sensitivity of the Compton scattering technique for identifying the number and type of electrons involved in the metal-insulator transition.

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Recent developments in spin-based electronics or spintronics have revived the interest in manganites $^1$. In particular, the bilayer manganites La$_{2-x}$Sr$_{1+2x}$Mn$_2$O$_7$ (LSMO) show interesting colossal magnetoresistance (CMR) effects $^2, 3$ in a complex phase diagram with charge and orbital ordering $^4$. As seen in Fig. 1 of Ref. $^3$, the compounds in the doping range $x = 0.3 - 0.4$ show a metal-insulator transition (MIT) associated with the onset of long-range ferromagnetic (FM) order. The MIT occurs at a Curie temperature $T_c$ of about 125 K (for $x = 0.35$) accompanied by colossal changes in the magnetoresistance $^2, 5$. Above $T_c$, the phase diagram displays an insulating paramagnetic (PM) phase. The Mn-3d electronic states, which are responsible for these properties, split into $e_g$ and $t_{2g}$ contributions in the crystal field of the MnO$_6$ octahedron. The FM phase below $T_c$ and its metallic conductivity are usually explained on the basis of the double exchange (DE) mechanism $^6$, where $e_g$ electrons hop between Mn sites through hybridization with the oxygen 2p orbitals and align the localized $t_{2g}$ spins by the exchange interaction. While the DE mechanism appears to capture the tendency towards ferromagnetism, it still remains unclear if oxygen orbitals should be explicitly included in the electronic degrees of freedom, or whether they can be integrated out as is often assumed in the standard models $^8, 9$.

Recent magnetic Compton scattering (MCS) studies $^{10}$ of the manganite FM phase have shown how the occupation numbers of the $e_g$ states vary with doping $^{11, 12}$ as well as temperature $^{13, 14}$. In addition, they have provided evidence for the coexistence of localized and itinerant $e_g$ magnetic electrons $^{15, 16}$ in the FM phase. MCS has also been used to study other spintronics materials such as magnetite Fe$_3$O$_4$ and its mysterious Verwey transition $^{17}$.

In this letter, we show that the anisotropy of high resolution Compton profiles (CP) displays a striking difference between the insulating PM and metallic FM case. This is important because this difference originates in the MnO planes which are the seat of the CMR properties. Similar effects have been observed in the metallic YBa$_2$Cu$_3$O$_7$ and insulating PrBa$_2$Cu$_3$O$_7$ systems $^{18}$. However, this is the first time that this effect has been observed on the same sample under the influence of external parameters such as temperature and magnetic field. We also provide a measure of the number of electrons involved in the CMR effect.

Compton scattering, or inelastic scattering with very
high momentum and energy transfer, is a probe of the ground state one-electron properties of the system [10]. The measured one-dimensional quantity $J(p_z)$ is a projection of the three-dimensional electron momentum density $\rho(p_x, p_y, p_z)$ onto the $z$-axis, which lies along the scattering vector:

$$J(p_z) = \int \int \rho(p_x, p_y, p_z)dp_xdp_y$$  \hspace{1cm} (1)

The sample used was a single crystal of La$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ with $x = 0.35$, which was melt-grown in flowing oxygen gas in a floating zone optical furnace [19]. According to the magnetic phase diagram determined by neutron-diffraction measurements, the present sample shows a ferromagnetic (FM) phase below 125 K [3]. High-resolution CP measurements were carried out with a Cauchois-type x-ray spectrometer installed on the BL08W beam line at SPring-8, Japan [19, 20, 21]. The energy of incident x-rays was 115.6 keV and the scattering angle was 170°. The momentum resolution is estimated to be 0.15 atomic units (a.u.). CPs along the [100] and [110] axes were measured in three different conditions: the FM metallic state at low temperature (20 K), the CMR state in an external field of 7 T, and the PM insulating state at 131 K (above $T_c$).

The electronic structure, momentum density, and the CPs along principal symmetry directions used for analyzing the present measurements have been computed within an all-electron, fully charge and spin self-consistent semi-relativistic KKR framework [23] for LaSr$_2$Mn$_2$O$_7$ in the I4/mmm [24] crystal structure [12]. Our computed electronic structure (for $x = 0.5$) is in good accord with other studies [25, 26]. The effects of doping $x$ have been included within a rigid band model. All calculations agree on a nearly or wholly halfmetallic FM band structure with the Fermi level crossing Mn $d$ bands.

Since the LSMO electronic structure has a two-dimensional character, we shall focus on the calculated (001) 2D-projection of the momentum density given by

$$\rho^{2d}(p_y, p_z) = \int \rho(p_x, p_y, p_z)dp_x.$$  \hspace{1cm} (2)

Apart from Fermi surface (FS) effects, the calculated distribution $\rho^{2d}(p_y, p_z)$ contains some anisotropic components produced by the wave functions of the $e_g$ and $t_{2g}$ electrons. We extract the $C_{4v}$ [27] anisotropy from $\rho^{2d}(p_y, p_z)$ by taking the difference

$$A^{2d}_{C_{4v}}(p_y, p_z) = \rho^{2d}(p_y, p_z) - \rho^{2d}(\frac{p_y + p_z}{\sqrt{2}}, \frac{p_y - p_z}{\sqrt{2}}).$$  \hspace{1cm} (3)

The subtraction in Eq. (3) acts as a projector on the $e_g$ and $t_{2g}$ subspace with the advantage of eliminating the large isotropic contribution of the core and some irrelevant valence electrons. The anisotropy $A^{2d}_{C_{4v}}(p_y, p_z)$ shown in Fig. 1 displays a strong peak near (0.7, 0.7) a.u. which arises from wavefunctions of $t_{2g}$ symmetry. On the other hand, there are peaks on the [100] axes at a distance of about 1.5 a.u. possessing $e_g$ character and smaller peaks in between 0.4 and 0.5 a.u. due to the oxygen $p$ states at the FS. These oxygen $p$ states hybridize with the $e_g$ states of Mn. The amplitude of the $t_{2g}$ and $e_g$ peaks is about 9% of $\rho^{2d}(0,0)$ while the amplitude of the $p$ related peaks is less than 4%. As $A^{2d}_{C_{4v}}(p_y, p_z)$ integrates to zero, it assumes positive and negative values.

Interestingly, Fig. 1 displays the same sharp FS features, which appear in the calculated 2D-projection of the spin momentum density onto the (001) plane [14]. In the present case, because of the definition of $A^{2d}_{C_{4v}}(p_y, p_z)$, we also have FS signatures rotated by 45° with respect to the original FS: These features come from the subtraction of the rotated 2-dimensional distribution in Eq. (3). The large nested portions of the FS seen in Fig. 1 give maxima in the generalized charge susceptibility [28] and explain the interplay of the conduction electrons and lattice vibrations which contribute to the MIT [29]. However, our aim here is not to investigate these FS properties in detail but rather to show how Compton spectroscopy may be used to study bonding effects across the MIT in the bilayer manganites. In order to analyze bonding effects we now discuss the CP anisotropy [30], i.e., the difference between CPs measured in two crystallographic directions. In the present case, we consider

$$A^{1D}(p_z) = J_{100}(p_z) - J_{110}(p_z).$$  \hspace{1cm} (4)

Recalling from Eq. (1) that the CP involves a double in-
tegral, or equivalently, a 1D-projection of the momentum density, the shape of $A^{1D}(p_z)$ can be computed from the 1D-projection of the previous two-dimensional anisotropy $A^{2d}_{C_{4v}}(p_y, p_z)$ as

$$A^{1D}(p_z) = \int A^{2d}_{C_{4v}}(p_y, p_z) dp_y.$$  \hspace{1cm} (5)

In Fig. 2 the profile $A^{1D}(p_z)$ shows the signatures of both the $t_{2g}$ peak (at about 0.7 a.u.) and the $e_g$ peak (at about 1.6 a.u.) discussed earlier and visible in Fig. 1. Fig. 2 shows that at low momenta the anisotropy of the MCP $A^{1D}_{mag}(p_z)$ (mostly of Mn-$d$ character) is markedly different from $A^{1D}(p_z)$. Clearly, the non-magnetic contribution due to the oxygen atoms is expected to give a more important impact at low momenta.

Next, we compare the calculated CP anisotropy with our measurements. In Fig. 3 all the metallic $A^{1D}(p_z)$ look remarkably alike, showing that the overall description of the electronic structure is satisfactory. In particular, the amplitude of $A^{1D}(p_z)$ in the resolution-broadened theory is the same as that in the experiment while in the case of the cuprates the theoretical $A^{1D}(p_z)$ had to be scaled down by a factor of 1.4 to obtain agreement with experiment [18]. The experimental curve for the insulator (paramagnetic phase), however, presents important changes in the low-momentum region indicating that the electrons with $p$ oxygen character at the FS structure near (0.5, 0) a.u. in Fig. 1 are significantly affected by the MIT. Moreover, the anisotropy for the insulator has a more pronounced positive excursion for $p > 4$ a.u. This feature at high momenta is rather small in amplitude but it makes the integrated anisotropy to be zero. These changes in $A^{1D}(p_z)$ can be explained in terms of a transition from metallic to admixed ionic-covalent Mn-O bonding [21]. According to the double-exchange mechanism [5], if the oxygen ion separates ferromagnetically coupled Mn$^{3+}$ and Mn$^{4+}$ in a lattice of disordered Mn ions, the state Mn$^{3+}$-O-Mn$^{4+}$ is degenerate with the state Mn$^{4+}$-O-Mn$^{3+}$ so that the $d$ electrons develop a long range phase coherence by hopping between Mn sites [7]. Therefore, in the FM phase below $T_c$, the bonding is metallic while in the PM phase above $T_c$ the bonding becomes admixed ionic-covalent. The latter is described by a short-range phase coherence.

The wavefunction localization effects across the MIT can also be monitored by studying the power density [18]

$$P_D(z) = \left| \int dp_z A^{1D}(p_z) \exp(ip_z z) \right|^2.$$  \hspace{1cm} (6)

The power density of the anisotropy separates in real space the different length scales contributing to the oscillations in the anisotropy in momentum. Thus, the peaks in the power density $P_D(z)$ indicate characteristic distances over which wave functions are coherent in given crystallographic directions. Figure 4 shows that the experimental data for the metallic phases and the theory are in agreement and that the wave functions are of a delocalized nature. However, the experiment for the insulator shows a clear tendency to shift spectral weight towards short distances. Thus, the localization trend for the insulator wave functions becomes clear. To ease the comparisons we have normalized all the power spectra to a unit area in Fig. 4 since only the relative weights in the same spectrum are relevant to study the localization [18].

The number of electrons involved in this localization can be extracted from the area enclosed by the anisotropy
difference
\[ \Delta A^{1D}(p_z) = A^{1D}_{FM}(p_z) - A^{1D}_{PM}(p_z), \]
where \( A^{1D}_{FM}(p_z) \) is a metallic anisotropy (FM or CMR) and \( A^{1D}_{PM}(p_z) \) is an insulating anisotropy. Therefore the quantity \( n_e \) given by
\[ n_e = \frac{1}{2} \int dp_z |\Delta A^{1D}(p_z)|, \]
measures the number of electrons whose wave functions change across the MIT. This is due to the shift of plane wave components from low to high momenta resulting in the wave function localization. We have normalized \( n_e \) to obtain the number of displaced electrons per Mn atom. The calculated values of \( n_e \) correspond to a displacement of 0.71 electron per Mn for the low-T FM-PM transition and of 0.67 electron per Mn for the CMR-PM transition. These values are calculated from the anisotropies between 0 and 9 a.u. Their error is ±0.08 based upon the statistical errors of the profiles. Thus, the present MIT gives particularly strong and robust signatures in momentum space.

In conclusion, our study shows that high-resolution Compton scattering spectra display striking features of the MIT and provide unique insights into the PM phase and the CMR effect in manganese. Ferromagnetism and metallic conductivity in the CMR phase are explained in terms of \( c_\sigma \) long range phase coherence produced by the DE mechanism. The momentum density anisotropy reveals that both the Mn and the oxygen orbitals play a key role in the MIT. By measuring the number of displaced electrons \( n_e \) across the MIT, the present method opens new opportunities for studying quantitatively the phase diagrams of complex materials.

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