Extracting d-orbital occupancy from magnetic Compton scattering in bilayer manganites

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1. INTRODUCTION

The double-layered manganites $La_{2-x}Sr_xMn_2O_7$ have drawn a great deal of attention as model systems that display a wide range of transport and magnetic properties and undergo a variety of phase transitions as a function of temperature, doping and magnetic field. In $La_{1.2}Sr_{1.8}Mn_2O_7$ (i.e., $x = 0.40$), investigated in this study, the CMR effect is a factor of $\sim 200$ at $129$ K (just above the Curie temperature $T_C$ $\sim 120$ K) under a magnetic field of $7$ T, and even at low fields the resistance changes by $\sim 200\%$. Neutron studies in this compound show that below $T_C$, the spins are aligned ferromagnetically within the MnO planes, but are canted antiferromagnetically between adjacent Mn-O planes.

Compton scattering refers to inelastic x-ray scattering in the deeply inelastic regime and it is well known that this technique directly probes the ground state momentum density $\rho(p)$ of the many body electronic system through a measurement of the so-called Compton profile, $J(p_z)$, where $p_z$ is the momentum transferred in the scattering process. X-rays interact not only with the electron charge but also with the electron spin. Therefore, the majority (minority) spin Compton profile $J_\uparrow$ ($J_\downarrow$) can be extracted by measuring two Compton scattering cross sections: one with the direction of the magnetization of the specimen parallel to the scattering vector, and the other with the magnetization anti-parallel. Thus, in ferro- or ferrimagnetic materials one can zoom in on the magnetic properties via the magnetic Compton profile (MCP) $J_{mag}(p)$ obtained by taking the difference between spin up (majority) and spin down (minority) Compton profiles

$$J_{mag}(p_z) = J_\uparrow(p_z) - J_\downarrow(p_z).$$

$I_{mag}$ can be expressed in terms of a double integral of the spin density, $\rho_{mag}(p)$ as

$$J_{mag}(p_z) = \int \int \rho_{mag}(p)dp_xdp_y,$$

where $\rho_{mag}(p) \equiv \rho_{\uparrow}(p) - \rho_{\downarrow}(p)$. The possibility of using magnetic Compton scattering (MCS) to determine the momentum distribution of magnetic electrons was recognized quite early, but since the scattering cross-section in the magnetic channel is typically several orders of magnitude smaller than for charge scattering, MCS experiments have become practical only in the last few years with the availability of high-energy, circularly polarized, X-rays at the synchrotron light sources.

In a recent MCS study of $La_{1.2}Sr_{1.8}Mn_2O_7$, we have focused on the $[110]$ MCP and shown that the shape of the $[110]$ MCP contains a remarkable signature of the occupancy of the $d_{x^2-y^2}$ electrons. By using a high magnetic field of $7T$ to maintain an electronically homogeneous ferromagnetic phase, we demonstrated that variations in the occupancy of the $d_{x^2-y^2}$ orbitals can be added from the $[110]$ MCPs measured at different temperatures. The purpose of the present article is to expand on the discussion of Ref. concerning how the shape of the $[110]$ MCP can be analyzed in terms of the reciprocal form factor.

We consider the shape of the magnetic Compton profile (MCP), $J_{mag}(p_z)$, in $La_{1.2}Sr_{1.8}Mn_2O_7$ for momentum transfer $p_z$ along the [110] direction and the associated reciprocal form factor $B(r)$ defined by the one-dimensional Fourier transform of $J_{mag}(p_z)$. $B(r)$ is shown to contain a prominent dip at $r \approx 1$ Å, where the minimum value $B_{min}$ of $B(r)$ can be correlated to the occupancies of the $e_g$ orbitals of $d_{x^2-y^2}$ and $d_{z^2}$ symmetry in the system. We illustrate our procedure in detail by analyzing the measured MCP at 5K and the MCP computed within the framework of the local spin density approximation (LSDA) and comment on the differences between the measured and computed $e_g$ occupancies as a reflection of the limitations of the LSDA in treating electron correlation effects.
B(r), which is related to the MCP via a one-dimensional Fourier transform along the direction of the scattering vector. In this connection, detailed forms of the relevant B(r) functions for various t_{2g} and e_{g} orbitals are given and their characteristic behavior with r is delineated. Since our purpose is to illustrate the fitting procedure for interpreting the shape of the B(r), we only discuss the experimental B(r) at 5K and the corresponding theoretical curve obtained using the local spin density approximation (LSDA). We also comment on the discrepancies between these computed and measured B(r)'s as a reflection of the shortcomings of the LSDA in treating electron correlation effects.

Concerning other MCP studies of the La-manganite, Koizumi et al. have investigated the doping dependence of the [100] and [001] MCPs under a relatively low magnetic field of 2.5 T. They analyze their MCPs in terms of atomic and cluster type computations of the momentum density to gain insight into the occupation of magnetic orbitals in the system. All existing MCP data on the double-layered manganite have been taken at a momentum resolution of around 0.4 a.u. Recently, Mijnarends et al. have investigated the MCPs in La-manganite along the three high symmetry directions and have shown that the resolution of about 0.4 a.u. is not sufficient for investigating Fermi surface signatures in the MCPs.

This article is organized as follows. Section II gives some technical details of our LSDA-based MCP computations and briefly introduces the B(r) function which is the basis of our analysis. Section III presents and discusses the details of how we analyze and fit the B(r) function. Section IV makes a few concluding remarks. As already indicated, in this article we only discuss the 5 K measurements taken under a magnetic field of at 7T; for technical details of the experimental measurements, the reader is referred to Refs. 7 and 8.

II. COMPUTATIONAL DETAILS

In order to obtain momentum densities and Compton profiles, the electronic structure of LaSr$_2$Mn$_2$O$_7$ was first obtained within an all-electron charge and spin self-consistent KKR framework. The reader is referred to Refs. 12, 13, 14, 15 for details of our band structure computations. The formalism for computing momentum densities is discussed in Refs. 16, 17, 18, 19. The lattice data were taken from Seshadri et al. Exchange-correlation effects were incorporated within the local spin density approximation (LSDA). Doping effects were treated within the rigid band approximation where the band structure of La$_{2-x}$Sr$_x$Mn$_2$O$_7$ is assumed to be the same as that of LaSr$_2$Mn$_2$O$_7$. More specifically, we have modeled the doped system by adjusting the Fermi energy $E_F$ in the majority spin band to accommodate the proper number of electrons for the $x = 0.4$ case.

A prominent feature of the band structure is the presence of a large exchange splitting on Mn, which yields a nearly unoccupied minority spin Mn-3d band. An analysis of the density of states shows that the $t_{2g}$ states lie at a binding energy of about 1 eV, while the $e_g$ states are placed essentially at the Fermi energy. Therefore our ab-initio calculation is consistent with molecular models which give a splitting of about 1 eV between the $t_{2g}$ and $e_g$ levels. We should keep in mind however that in a band structure scheme the $t_{2g}$ and $e_g$ characters of Bloch wavefunctions vary continuously across various bands and that there is no strict gap between these levels for either the majority or the minority bands.

If we assume that the 3.6 Mn electrons effectively retain their atomic character, then we would expect that these electrons will occupy the up-spin states following Hund’s first rule. In particular, the first three electrons will go into the three lower lying up-spin $t_{2g}$ orbitals $(d_{xy}, d_{xz}, d_{yz})$, while the remaining 0.6 electrons will occupy the $e_g$ orbitals $(d_{x^2-y^2}, d_{3z^2-r^2})$. Moreover, since the $t_{2g}$ and $e_g$ states are separated by a large energy gap of about 1 eV, which is much larger than $kT$, the occupancy of $t_{2g}$ states will change little with T, and the effect of temperature will mainly be to redistribute the 0.6 $e_g$ electrons between the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals. A more quantitative handle on the occupancy of magnetic orbitals can be obtained in favorable cases by considering the reciprocal form factor, B(r), which is defined as the Fourier transform of the spin momentum density:

$$B(r) = \int \rho_{\text{mag}}(p) \exp(-ip \cdot r)dp.$$

We now express $\rho_{\text{mag}}(p)$ as a sum over the momentum densities of the molecular orbitals $\psi_i^{MO}(p)$ of the magnetic electrons, weighted by their occupancies $n_i$:

$$\rho_{\text{mag}}(p) = \sum_i n_i |\psi_i^{MO}(p)|^2.$$

By transforming Eq. 4 into real space, it is straightforwardly shown that

$$B(r) = \sum_i n_i \int \psi_i^{MO}(s) \psi_i^{MO}(s + r) ds,$$

where the integrals on the right hand side give the autocorrelation of the magnetic orbitals, $\psi_i^{MO}(r)$, i.e. the overlap between $\psi_i^{MO}(s)$ and the same orbital translated by a distance r. Alternatively, $B(r)$ along a given direction can be obtained directly from Eq. 5 by taking the 1D-Fourier transform of the MCP along that direction. By modeling the right hand side of Eq. 4 and comparing the results to the experimentally determined $B(r)$, insight into the occupation numbers $n_i$ can then be obtained.
model $B(r)$ using Slater type orbitals (STOs) \(^{27,28}\). The STO of $xy$ symmetry for example is given by

$$\psi_{xy} = N \ xy \ \exp(-\xi r),$$

where $\xi$ is the exponent and $N$ is the normalization factor. Other STOs are of similar form with the factor of $xy$ in Eq. (6) replaced by one of a different symmetry. The overlap integral in Eq. (6) for various STOs is easily computed. The analytic form of the result is:

$$B_{t2g} = e^{-t} \left( 3 + 3t + t^2 - \frac{11t^4}{140} - \frac{t^5}{84} + \frac{t^6}{420} \right),$$

$$B_{x^2-y^2} = e^{-t} \left( 1 + t + \frac{2t^2}{7} - \frac{t^3}{21} - \frac{t^4}{21} - \frac{t^5}{105} \right),$$

$$B_{3z^2-r^2} = e^{-t} \left( 1 + t + \frac{8t^2}{21} + \frac{t^3}{21} - \frac{t^4}{140} - \frac{t^5}{1260} + \frac{t^6}{1260} \right),$$

where

$$t = \frac{\xi r}{Z_{eff} / 3}r,$$

and $Z_{eff}$ denotes the effective nuclear charge (all the quantities are implicitly in atomic units). Note that we have grouped the contributions of the three different $t_{2g}$ orbitals ($xy$, $yz$, and $zx$) into a single quantity $B_{t2g}$ in Eq. (6) for convenience. By choosing an occupancy of 3 for the $t_{2g}$ states, of $f$ for the $d_{x^2-y^2}$ and $(0.6-f)$ for the $d_{3z^2-r^2}$ state, the total $B(r)$ is given by

$$B(r) = \frac{B_{t2g}(r) + fB_{x^2-y^2}(r) + (0.6-f)B_{3z^2-r^2}(r)}{3.6},$$

where we have imposed the condition $B(0) = 1$ since we compare MCPs normalized to one.

Figures 2 and 3 provide insight into the modeling of $B(r)$ based on Eqs. 6-11. Figure 2 shows the behavior of individual contributions $B_{t2g}$, $B_{x^2-y^2}$, and $B_{3z^2-r^2}$, while Fig. 3 delineates the variations in the dip around $r \approx 1$ Å as a function of the occupancy $f$ of the $d_{x^2-y^2}$ orbital. We have chosen $Z_{eff} = 1$ in all calculations in this article. It is clear from Eq. (10) that $Z_{eff}$ is a scaling parameter. Its precise value is not so important for our analysis since it merely serves to shift the position of the minimum in $B(r)$, but does not affect the size of the dip in $B(r)$ which is our main concern. The key result of our analysis is that the dip in $B(r)$ in Fig. 3 which arises from the contributions in $t^4$ and $t^6$, is produced mainly by the autocorrelation of the $d_{x^2-y^2}$ orbital. The $d_{3z^2-r^2}$ orbital is seen from Fig. 3 to give a positive contribution near 1 Å. With regard to the individual terms from the $xy$, $yz$ and $zx$ orbitals to $B_{t2g}$ (not shown in Fig. 2), the $d_{xy}$ orbital gives a small positive contribution, while the $d_{xz}$ and $d_{yz}$ orbitals give negative contributions.

### III. RESULTS AND DISCUSSION

Figure 1 compares the $B(r)$ along [110] obtained by using Eq. (6) from the measured MCP with the corresponding result from the computed MCP based on the LSDA. Our focus is on understanding the nature of the pronounced dip around $r \approx 1$ Å, which is seen in both theory and experiment. In order to interpret this minimum in terms of occupancy of magnetic orbitals, we
The minimum value $B_{\text{min}}$ of $B(r)$ along [110] is seen from Fig. 3 to be correlated with the $d_{x^2-y^2}$ occupancy given by $f$. The inset to Fig. 3 in fact shows that $B_{\text{min}}$ can be fitted linearly:

$$B_{\text{min}} = af + b,$$

(12)

where $a = -0.130$ and $b = 0.004$. The sketch of the $d_{x^2-y^2}$ orbital in Fig. 3 is perhaps helpful in this regard: when the $d_{x^2-y^2}$ orbital is translated along [110], the positive and negative lobes will overlap and yield a negative dip at a distance of the order of orbital dimensions. Finally, we note that in writing Eq. 11 for $B(r)$, we have not included the effect of finite experimental resolution on the MCP. The finite resolution $\Delta p$ (FWHM) in momentum space (assuming a gaussian resolution function) leads to a multiplicative attenuation of $B(r)$ in $r$-space given by

$$B_a(r) = B(r) \exp(-r^2/S^2),$$

(13)

where

$$S = \frac{4\sqrt{\ln(2)}}{\Delta p}.$$  

(14)

For $\Delta p = 0.4$ Å, the exponential factor is 95% at $r = 1$ Å, therefore it has little effect on the value of $B_{\text{min}}$.

The minimum in the $B(r)$ curves of Fig. 4 can now be used to derive the occupancies of the $e_g$ orbitals. Using the fit of Eq. 12 we thus obtain for the LSDA curve of Fig. 1 $f = 0.35$, which implies occupancies of 0.35 and 0.25 for the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals, respectively. The corresponding values for the 5K experimental $B(r)$ of Fig. 1 are: 0.40 for $d_{x^2-y^2}$ and 0.20 for $d_{3z^2-r^2}$. This preferential occupation of the $d_{x^2-y^2}$ orbital is somewhat surprising since the Mn-O bond length for the apical O atoms is larger than that for the in-plane O atoms, and a simple molecular orbital scheme would suggest that the energy of the antibonding $d_{3z^2-r^2}$ level will be lowered in relation to that of the $d_{x^2-y^2}$ level. Note, however, that electron correlations beyond the LSDA are needed to stabilize the canted antiferromagnetic order between the two Mn-O planes observed in the absence of an external magnetic field. The occupancy of the $d_{3z^2-r^2}$ orbital promotes ferromagnetism so that antiferromagnetic correlations will tend to reduce the $d_{3z^2-r^2}$ population. Reference 5 argues that the on-site Coulomb correlation $U$ of Mn $d$ electrons can produce a significant splitting of the $e_g$ states, modify interlayer exchange interactions and magnetic ordering, and promote anisotropy in the electrical transport by reducing the conduction along the $c$-axis. Bearing all this in mind, we consider the discrepancy between the depth of the minimum between the LSDA and experiment in Fig. 1 to reflect the presence of electron correlation effects beyond the LSDA framework underlying our computations.

Turning to the behavior of $B(r)$ beyond the dip around $r = 1$ Å, Fig. 1 shows the presence of long range oscillations in the experimental $B(r)$ as well as the corresponding LSDA calculations (damping effect of the resolution notwithstanding). These oscillations at large $r$ are absent in our relatively simple STO-based model as seen from Fig. 3. We emphasize that sizable values of $B(r)$ beyond atomic dimensions are a hallmark of electronic states extending over larger distances as a result of the mixing of Mn and O orbitals in the MnO$_2$ planes. These hybridization effects are crucially important for faithfully modeling the shape of the MCP in a global sense. Our relatively simple STO-based model is not meant to reproduce such a global fit to the MCP, but to only highlight the atomic-like features hidden in the MCP via the use of $B(r)$ function at low $r$-values. As we have already pointed out, when the x-ray scattering vector lies along the [110] direction, the number of magnetic electrons of a specific symmetry, i.e., $d$-electrons of $x^2-y^2$ symmetry, yield a distinct atomic signature in the $B(r)$, allowing us to extract the occupancies of the $e_g$ electrons.

IV. SUMMARY AND CONCLUSIONS

We discuss how the shape of the [110] MCP in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ can be analyzed in terms of the reciprocal form factor $B(r)$ given by the one-dimensional Fourier transform of the MCP. By interpreting $B(r)$ as the autocorrelation function of the ground state wavefunction, one can obtain a handle on the occupancies of various magnetic orbitals in the system. In particular, the $B(r)$...
along the [110] direction in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ contains a distinct dip at $r \approx 1$ Å and the value $B_{\text{min}}$ of $B(r)$ at the minimum can be related directly to the occupancy $f$ of the $d_{x^2-y^2}$ orbital as: $B_{\text{min}} = a f + b$, where $a = -0.130$ and $b = 0.004$. The specific forms of the $B(r)$ functions associated with various $t_{2g}$ and $e_g$ Slater-type orbitals are presented and used to analyze $B(r)$ functions for the 5K MCP data and the computed MCP based on the LSDA as illustrative examples. In this way, for LSDA we deduce $f = 0.35$ or occupancies of 0.35 for $d_{x^2-y^2}$ and 0.25 for $d_{3z^2-r^2}$ orbitals; the corresponding occupancies derived from the experimental 5K MCP are 0.40 for $d_{x^2-y^2}$ and 0.20 for the $d_{3z^2-r^2}$ orbital. The larger experimental value of the $d_{x^2-y^2}$ occupancy reflects limitations of the LSDA in accounting for electron correlation effects in the system. Our approach would allow a determination of the occupancies of magnetic orbitals through an analysis of the shapes of the MCPs more generally in complex materials.

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