Orbital Order at Mn and O Sites and Absence of Zener Polaron Formation in Manganites

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(Received 5 June 2009; published 28 August 2009)

We report the doping dependence of the ground state of A-site ordered manganites below and above half doping. Energy and polarization dependence of the orbital reflection, taken by resonant soft-x-ray powder diffraction, at both Mn L2,3 and O K edges, provides direct evidence for orbital order at Mn3+ and oxygen sites and absence of Zener polaron formation. For x ≳ 0.2 anomalous melting of the orbital order is observed, which is coupled neither to magnetic ordering nor to a structural transition, indicating a two-dimensional character of the interactions.

DOI: 10.1103/PhysRevLett.103.097205 PACS numbers: 75.25.+z, 71.30.+h, 75.47.Lx

Interplay between electron, spin, charge, orbital, and lattice degrees of freedom in doped manganites (perovskites $ABO_3$ where $B = \text{Mn}$) can lead to a variety of charge and magnetic ground states, ranging from states with colossai magnetoresistance to charge and orbital ordering [1].

Recently it has been proposed that phases other than the checkerboard charge and orbital ordering pattern, which is characterized by the alteration of Mn3+ and Mn4+ sites (Mn-centered charge ordering), might be present in manganites close to half doping. Another “charge-ordering” pattern has been predicted where the charge is localized on the Mn-O bonds (bond-centered charge ordering) [2]. This type of model would allow Zener polaron-type phases, reflected by dimerized type spins aligned ferromagnetically. Besides the two pure ordering states, where the charge is localized either on the $3d$ ion sites or on the bonds, an intermediate phase that combines both features might exist and would lead to the existence of different magnetic states such as simple ferromagnetism ($F$) and antiferromagnetic ($G$) and more complicated $A$-, $C$-, and $CE$-type antiferromagnetic order [2]. On the experimental side, the occurrence of Zener polaron-type phases in manganites with broken Mn-site symmetries remains a controversial issue [3–6].

In this broadened and more complex view of possible ground states of manganites close to half doping, the role of the oxygen 2p states has become very important. In a recent work, ordering of the oxygen 2p states of $\text{La}_{0.78}\text{Sr}_{0.22}\text{Mn}_2\text{O}_3$ and $\text{Bi}_{0.33}\text{Ca}_{0.67}\text{Mn}_2\text{O}_3$ was directly probed by resonant diffraction at the O K edge [7]. It was shown that the role of the oxygen can change dramatically from one compound to another. Whereas charge ordering of “spherical” holes at the oxygen is found in $\text{La}_{0.78}\text{Sr}_{0.22}\text{Mn}_2\text{O}_3$, a pure orbital ordering arising from the hybridized orbitally ordered metal $3d$–oxygen 2p states occurs in $\text{Bi}_{0.33}\text{Ca}_{0.67}\text{Mn}_2\text{O}_3$.

Increase of A-site randomness augments the magnetoresistance effect, decreases the charge order (CO) and orbital order (OO) temperature $T_{\text{CO/OO}}$, and also makes the charge-spin-orbital correlation short-ranged [8–10]. To quantify the effect of the quenched disorder on the colossal magnetoresistance physics, the study of the A-site ordered manganite ($\text{R}_1\text{−}_\text{Ca}_\text{BaMn}_2\text{O}_6$, where the (R, Ca) and Ba are located on planes alternating along the c axis, is extremely important. The high temperature crystal structure of the cation-ordered material is of the $a_p \times a_p \times 2a_p$ type with $a_p = 3.9$ Å the cubic perovskite unit cell parameter. A previous study of the half-doped system ($x = 0$) SmBaMn$_2$O$_6$ found $T_{\text{CO/OO}} = 360$ K and an antiferromagnetic transition at $T_N = 250$ K followed by a reorientation of the orbital order at $T_{\text{CO/OO}} = 200$ K [8]. Resonant soft-x-ray powder diffraction showed that this system has an OO of $e_\parallel$ electrons with $[\rho_2 - \rho_3]a_\perp$ type in contrast to the layered $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_4$ with $[\rho_3 - 2\rho_2]a_\perp$ type [11]. This difference in the $e_\parallel$ level occupation is believed to arise from the difference in the crystal structure of the two compounds. The doping dependence of the ordering wave vector of the orbital reflection $q = (\delta_x, \delta_y, 0)$ was found to depend linearly on $x$ with $\delta = (1-x)/4$ for doping contents above half doping, and to be constant $q = (\delta_x, \delta_y, 0) = (1/4, 1/4, 0)$ below [8].

In this Letter we study the ground state of A-site ordered manganites beyond the half-doping case with resonant soft-x-ray and neutron-powder diffraction. The results clarify the role of the oxygen 2p states and relate the anomalous melting of OO to a reduction of the three-dimensional electron coupling for higher doping due to the random stacking along the c axis.

$\text{ Tb}_{1-x}\text{Ca}_x\text{BaMn}_2\text{O}_6$ and $\text{ TbBa}_{1-x}\text{La}_x\text{Mn}_2\text{O}_6$ compounds were synthesized following the same procedure as in Ref. [11]. Resonant soft-x-ray diffraction experiments...
were performed on the RESOX [12] end station at the SIM beam line of the Swiss Light Source of the Paul Scherrer Institut (PSI), Switzerland. Polycrystalline pellets of 10 mm diameter were glued onto a copper sample holder mounted on a He flow cryostat which achieved temperatures between 10 and 400 K. Experiments were performed using light with linear horizontal or vertical polarization leading to \( \pi \) or \( \sigma \) incident photon polarization in the horizontal scattering geometry, respectively. Two-dimensional data sets were collected with a commercial Roper Scientific charge-coupled-device (CCD) camera mounted in a vacuum. The sections of the resonant orbital powder-diffraction rings measured with the CCD camera are integrated along the vertical direction and fitted with a pseudo-Voight function. This results in the integrated intensity, the position in \( 2\theta \), and the background corresponding to the fluorescence. Neutron-powder-diffraction measurements were carried out at the high-resolution HRPT diffractometer [13] at the SINQ spallation neutron source of the Paul Scherrer Institut, Switzerland. The high intensity mode of HRPT was used with the neutron wavelength = 1.49 Å. The refinements of the crystal structure parameters were performed using FULLPROF [14].

The energy dependence of the integrated intensity of the orbital reflection \( (\delta_x, \delta_z, 0) \), where \( \delta = \delta(x) \), for \( x > 0 \) and \( (1/4, 1/4, 0) \) for \( y = 0.1 \) in the vicinity of the Mn \( L_{2,3} \) edges, normalized to the main feature, is shown in Fig. 1. The linear dependence of \( \delta \) with the doping seen in Ref. [8] is confirmed by our measurements (Fig. 2). Apart from the changes on \( \delta \), there is a distinct trend in the shape of the spectra with doping indicating a change of the electronic Mn states. The most visible change is that the intensity of the \( L_2 \) edge (features \( D, E, F \)) gets more intense upon doping, while feature \( C \) gets broader in comparison to features \( A \) and \( B \). These changes contrast with the simple view that doping merely produces a dilution of Mn\(^{3+}\) by Mn\(^{4+}\) ions, leading to the linear behavior of \( \delta(x) \) which would keep the energy dependence unchanged to first order.

To clarify the role of the oxygen \( 2p \) states in these electronic changes observed as a function of doping, the energy dependence of the orbital reflection \( (\delta_x, \delta_z, 0) \) was measured in the vicinity of the oxygen \( K \) edge for \( x \approx 0.2 \) [Fig. 2(a)]. Note that for \( x < 0.2 \) the orbital reflection cannot be accessed due the long wave-length of the x-ray radiation at the oxygen \( K \) edge. The occurrence of a diffraction peak with a narrow resonance for the same propagation vector that reflects the OO on the Mn\(^{3+}\) is direct proof of the ordering of the empty O \( 2p \) states. The \( 1s \to 2p \) resonance at the O \( K \) edge is well described by a single harmonic oscillator function. Measurements with different incident polarizations, \( \sigma \) and \( \pi \), are equal within experimental accuracy at both Mn \( L_{2,3} \) and O \( K \) edges for all accessible doping contents, as exemplified in Fig. 2(b) for \( x = 0.4 \) and \( x = 0.1 \). Intensities independent of polarization indicate that the scattered radiation is purely rotated \((\sigma'\pi \text{ or } \pi'\sigma)\) as signals in the unrotated channels \((\sigma'\sigma \text{ and } \pi'\pi)\) are different in intensity due to their different dependence on the Bragg angle \( \theta \) [15]. The polarization behavior of the \((\delta_x, \delta_z, 0) \) reflection contains inherent information on OO and is consistent with the occurrence of orbital zigzag stripes. It indicates that at the O \( K \) edge the signal comes from an induced quadrupole, i.e., an OO reflection of O \( 2p \) states, and does not represent charge ordering at the oxygen ions with this wave vector, in contrast to predictions on cuprates [16]. The expression for the Bragg diffraction amplitude for this type of OO for the \((\delta_x, \delta_z, 0) \) reflection is

\[
F_{\sigma'\sigma}(\theta) = F_{\sigma'\pi}(\theta) = -2 \cos \theta (T_{2}^{0})^{y} \sin \psi \tag{1}
\]

with \( \psi \) the azimuthal angle and \( \langle T \rangle \) the atomic multipole reflecting an electron quadrupole \( T_{2}^{0} = \langle T_{2}^{+} \rangle^{y} + i\langle T_{2}^{-} \rangle^{y} \) [15]. Note that the comparison with the powder-diffraction data requires an integration of intensity over \( \psi \). For this case of OO, \( F_{\sigma'\sigma}(\theta) = F_{\sigma'\pi}(\theta) = 0 \). For Zener polaron-type ground states that have been proposed for those compounds, the inversion symmetry at the Mn is lost, as electrons are shared between different Mn sites. This loss of symmetry may lead to possible electric polarization of the material [3,17]. For a Zener polaron ordering the corresponding expressions for the diffraction amplitude for the four polarization channels are

\[
F_{\sigma'\sigma}(\theta) = \sqrt{6} \left[ -\frac{1}{\sqrt{2}} \langle T_{2}^{+} \rangle^{y} \sin(2\psi) + \frac{1}{2} \langle T_{2}^{-} \rangle^{y} [1 - \cos(2\psi)] \right], \tag{2}
\]
This is in strong contrast to Ref. [3], where from the reflection in the polarizations. The inset shows rebinned powder reflection (measured at the O

FIG. 2 (color online). (a) Energy dependence of the integrated intensity of the orbital reflection ($\delta_\tau$, $\delta_\pi$, $\delta_0$) of Tb$_{1-x}$Ca$_x$BaMn$_2$O$_6$ measured at the O $K$ edge for $x = 0.2$, 0.33 and $x = 0.4$ (see inset). For $x = 0.4$ this energy dependence is shown for $\pi$ and $\sigma$ incident polarizations together with the fluorescence. The inset shows the momentum dependence of the ordering wave vector. (b) Energy dependence of the $(0.225, 0.225, 0)$ orbital reflection of $x = 0.1$ measured at the Mn $L_{2,3}$ edges for $\pi$ and $\sigma$ incident polarizations. The inset shows rebinned powder reflection $(1/4, 1/4, 0)$ of TbBaMn$_2$O$_6$ collected with $\pi$ and $\sigma$ incident polarizations.

$$F_{\pi', \sigma}(\theta) = -\sqrt{2}(T^2_{\pi', \sigma})'' \sin^2 \theta \sin 2\psi$$

$$- (T^2_{\pi', \sigma})''(1 + \cos^2 \theta + \sin^2 \theta \cos 2\psi), \quad (3)$$

$$F_{\pi', \sigma}(\theta) = F_{\pi', \sigma}(-\theta)$$

$$= 2\left\{ \frac{1}{\sqrt{2}} \left[ \cos \theta(T^2_{\pi', \sigma})'' \cos \psi - \sin \theta(T^2_{\pi', \sigma})'' \cos 2\psi \right] \right.$$

$$- \cos \theta(T^2_{\pi', \sigma})'' \sin \psi + \frac{1}{2} \sin \theta(T^2_{\pi', \sigma})'' \sin 2\psi \right\}. \quad (4)$$

Equations (2) to (4) lead to a much more complex behavior with significantly different intensities for powder average of the $\sigma$ ($F_{\pi', \sigma} + F_{\pi', \sigma}$) and $\pi$ ($F_{\pi', \sigma} + F_{\pi', \sigma}$) incident polarization channels, inconsistent with our data. The same argument excludes the occurrence of the Zener polarons also in Bi$_{0.31}$Ca$_{0.69}$MnO$_3$ [7] and La$_{0.5}$Sr$_{0.5}$MnO$_3$ [18]. This is in strong contrast to Ref. [3], where from the magnetic structure of YBaMn$_2$O$_6$ a Zener polaron ordering was predicted. These authors [3] also claim that the magnetic neutron scattering is essentially the same in YBaMn$_2$O$_6$ and in TbBaMn$_2$O$_6$, and suggest no fundamental reason to distinguish the ground state of YBaMn$_2$O$_6$ from that of TbBaMn$_2$O$_6$.

In Fig. 3, the temperature dependence of the $(0.2, 0.2, 0)$ reflection in the Tb$_{0.8}$Ca$_{0.2}$BaMn$_2$O$_6$, measured at the O $K$ edge and at the Mn $L$ edge, is shown. Both signals follow clearly the same continuous dependence on temperature, giving evidence of the fact that the ordering of the oxygen $2p$ states is directly correlated to the charge and orbital order of the Mn $3d$ states, in contrast to what has been observed in the temperature dependence of the orbital signal in the half-doped system [11]. There, restacking of the OO along the $c$ axis shows up as a sharp increase in intensity for decreasing temperature (see Fig. 3). For a change in the restacking from AAAA disposition of the planes to AABB as is observed in the half-doped case [11], the intensity calculations predict a 25% change of intensity. The calculated change of intensity for other restackings is even larger. The observed continuous temperature dependence of the reflection rules against a restacking transition.

Interestingly, at the same temperature as the restacking is observed for the half-doped case ($x = 0$), for $x > 0$ the orbital ordering wave vector starts to depend on temperature as shown in Fig. 4 for $x = 0.33$. A temperature dependence of the orbital wave vector $\mathbf{q} = (\delta_\tau, \delta_\pi, 0)$ was also observed for Bi$_{0.31}$Ca$_{0.69}$MnO$_3$ [7] and Bi$_{0.53}$Sr$_{0.47}$MnO$_3$ [19], but occurring much closer to $T_{\text{OO}}$.

We have complemented these results with neutron powder-diffraction experiments to determine the temperature dependence of both the crystal and the magnetic structure.

FIG. 3 (color online). Comparison of the temperature dependence of the integrated ($\delta_\tau$, $\delta_\pi$, 0) reflection in Tb$_{0.8}$Ca$_{0.2}$BaMn$_2$O$_6$, taken at the O $K$ edge (528.4 eV) and Mn $L_3$ edge (643 eV) measured with $\pi$ incident polarization.
The evolution with temperature of the orbital wave vector \( \vec{q} \), expected solely from the temperature change of the unit cell parameters, is also shown in Fig. 4. The incommensurability of the orbital reflection observed in the resonant scattering experiments cannot be explained simply in terms of the changes of the \( a_p \times a_p \times 2a_p \) unit cell as a function of temperature and that its origin must be electronic rather than structural. Magnetic neutron powder-diffraction measurements that will be discussed in detail elsewhere show that the Néel temperature \( T_N \) is lower than the temperature at which the ordering wave vector gets temperature dependent. This indicates clearly that this anomalous melting of the orbital ordering is not directly correlated with the occurrence of magnetic order as proposed in [20], but is related to the instability driving the restacking transition at half doping (\( x = 0 \)).

The instability of the orbital order reflected by this anomalous melting behavior can be correlated to the \( e_g \) electron occupancy of the \([x^2 - y^2][y^2 - z^2]\) orbital in the \( A \)-site ordered manganite. These orbitals provide a coupling along the \( c \) axis that is supported by the three-dimensional perovskite crystal structure. However, this coupling is weakened for \( x > 0 \) due to the randomness of the stacking along the \( c \) axis. When the temperature increases, the volume of the unit cell also increases (see inset in Fig. 4). This will further reduce the coupling along \( c \), and consequently the orbitals will be more free to move in the plane. In addition, the frustration of the OO in the \( ab \) plane, which likely takes place for Ca contents \( x > 0 \), would induce a change on the OO unit cell as a function of temperature. The change on the orbital order wave vector as a function of temperature \( \vec{q}(T) \) (anomalous melting) is therefore due to a more two-dimensional character of the interactions due to the random stacking of \([x^2 - y^2][y^2 - z^2]\) orbitals along the \( c \) axis.

In conclusion, we present a resonant soft-x-ray powder-diffraction study on the doping dependence of \( A \)-site ordered manganites, complemented by powder neutron diffraction. The occurrence of orbital ordering on the Mn\(^{3+}\) \( 3d \) and O \( 2p \) states has been observed with electronic changes happening on the Mn\(^{3+}\) states upon doping. No Zener polaron ordering or charge ordering of oxygen ions was detected despite the occurrence of a resonant reflection at the oxygen \( K \) edge. This indicates clearly that more parameters than merely the doping content have to be taken into account in order to predict the appearance of new and different ground states. No visible restacking of the orbitals along the \( c \) axis was observed in contrast to the half doping. The anomalous melting of the OO, which is directly coupled neither with the magnetic ordering nor with a structural change, is controlled by the weakening of \( c \) axis coupling due to random stacking, getting the system more two dimensional.

We thank the beam line staff of X11MA for their excellent support and also Dr. L. Keller and Dr. D. Backes for their help during DMC measurements. This work was supported by the Swiss National Science Foundation and the NCCR MaNEP Project.