Nature of $e_g$ Electron Order in La$_{1-x}$Sr$_{1+x}$MnO$_4$

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Synchrotron x-ray scattering measurements of the low-temperature structure of the single-layer manganese oxide La$_{1-x}$Sr$_{1+x}$MnO$_4$, over the doping range 0.33 ≤ $x$ ≤ 0.67, indicate the existence of three distinct regions: a disordered phase ($x \leq 0.4$), a charge-ordered phase ($x \geq 0.5$), and a mixed phase (0.4 < $x$ < 0.5). For $x > 0.5$, the modulation vector associated with the charge order is incommensurate with the lattice and depends linearly on the concentration of $e_g$ electrons. The primary superlattice reflections are strongly suppressed along the modulation direction and the higher harmonics are weak, implying the existence of a largely transverse and nearly sinusoidal structural distortion, consistent with a charge-density wave of the $e_g$ electrons.

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Perovskite-derived transition metal oxides have attracted much attention over the past decade because of their unusual electronic properties. Strong electron correlations give rise to such phenomena as high-temperature superconductivity in layered cuprates and stripe-like order in layered cuprates and nickelates. In the case of the manganites, an additional strong coupling between charge and lattice degrees of freedom leads to a very rich electronic phase diagram in which crystallographic and magnetic structures as well as transport properties are intimately related. The competition among various phases has been closely associated with the colossal magnetoresistance (CMR) observed in these materials. For example, the perovskite La$_{1-x}$Ca$_x$MnO$_3$ exhibits two low-temperature phases at doping $x \sim 0.5$, one a ferromagnetic metal and the other an antiferromagnetic insulator [4, 5]. The insulating phase at the doping level $x = 0.5$, where there is on average half an $e_g$ electron per manganese atom, is characterized by a complex checkerboard arrangement of ordered $e_g$ electrons, orbitals and spins [6, 7]. The ordered phase of La$_{1-x}$Ca$_x$MnO$_3$ extends to rather high doping where the average number $n_e = 1 - x$ of $e_g$ electrons decreases markedly and, consequently, the low-temperature unit cell becomes very large [8, 9].

CMR has been observed in the perovskite and double-layer manganites, but not in the single-layer system [9, 10], the most nearly two-dimensional member of this series. Nevertheless, there are signs that the physics of La$_{1-x}$Sr$_{1+x}$MnO$_4$ is similar to that of the perovskite manganites. For example, similar antiferromagnetic order has been reported for La$_{0.50}$Sr$_{1.50}$MnO$_4$ [11]. Moreover, the low-temperature phase is sensitive to magnetic fields [12] and it extends to high doping (low $e_g$ electron concentration) [13]. A systematic study of the low-temperature structural phases of La$_{1-x}$Sr$_{1+x}$MnO$_4$ should provide valuable insights into the effect of dimensionality on the properties of the manganites. Such a study may also contribute to a deeper understanding of the single-layer transition metal oxides.

In this Letter, we report a non-resonant x-ray scattering study of La$_{1-x}$Sr$_{1+x}$MnO$_4$ (0.33 ≤ $x$ ≤ 0.67). We first consider the low-temperature structure of La$_{0.50}$Sr$_{1.50}$MnO$_4$. Our data provide a more complete picture than previous neutron [11] and x-ray [13] scattering experiments. We then extend our investigation to study the effects of varying the $e_g$ electron concentration in the MnO$_2$ layers. We find three distinct regions: disordered ($x \leq 0.4$), mixed-phase (0.4 < $x$ < 0.5), and charge-ordered ($x \geq 0.5$). Above $x = 0.5$, the ordering of $e_g$ electrons results in a structural distortion whose modulation period only depends on $n_e$. The distortion is largely transverse and nearly sinusoidal, consistent with charge-density-wave order of the $e_g$ electrons.

Samples of La$_{1-x}$Sr$_{1+x}$MnO$_4$ were prepared from stoichiometric amounts of La$_2$O$_3$, MnO$_2$, and SrCO$_3$ powders. The mixtures were calcined three times for twelve hours between 1300°C and 1360°C. The calcinated powders were then pressed into rods of 5mm diameter and sintered at 1600°C for twelve hours. Single crystals were grown by the floating-zone method at a rate of 6mm/hour in an oxygen atmosphere of 5bar. Crystal pieces of dimensions 2x4x11mm$^3$ were cut from the grown boules and were mounted inside a closed-cycle refrigerator. The mosaic widths of the crystals used in this study were 0.02 – 0.06° full width at half maximum (FWHM). The data were collected using a four-circle diffractometer at beamline 7-2 of the Stanford Synchrotron Radiation Laboratory. A monochromatic x-ray beam was obtained from the wiggler spectrum via a Si (111) double-crystal monochromator. In order to study the bulk structure, an x-ray energy of 14keV was selected, providing a penetration depth of about 40µm.

The low-temperature phase of La$_{0.50}$Sr$_{1.50}$MnO$_4$ was probed extensively via scans along the high-symmetry directions in reciprocal space. Two such scans are pre-
presented in Fig. 1. The essential features of the ordered structure do not change below the charge-ordering temperature $T_{CO} \approx 240$K. In addition to the peaks present in the high-temperature ($I4/mmm$) structural phase (henceforth referred to as high-symmetry peaks), peaks with wavevectors $(\frac{1}{2}, \frac{1}{2}, 0)_t$ and $(\frac{1}{4}, \frac{3}{4}, 0)_t$ were found (the subscripts $t$ and $o$ indicate, respectively, the tetragonal and orthorhombic unit cells). The $(\frac{1}{4}, \frac{1}{4}, 0)_t$ peaks ($h$-odd peaks in the orthorhombic notation used in Fig. 1) suffer a near extinction along $(h, h, 0)_o$ ($((h, 0, 0)_o$ in orthorhombic notation). The presence of a quarter-wave modulation has been reported in electron diffraction measurements [7, 10]. A neutron diffraction study found only a half-wave modulation and concluded that the quarter-wave modulation seen in electron diffraction comes from a surface phase [1]. The measurements reported here were performed at relatively high x-ray energy (14keV) to achieve a bulk penetration depth and were reproduced on samples from three different growths. Moreover, preliminary neutron diffraction on a larger sample with mosaic width of about 0.2° (FWHM) has confirmed the presence of the quarter-wave peaks in the bulk.

The existence of a quarter-modulation wavevector along $(h, h, 0)_t$ seems to imply that the $a$ and $b$ axes of the low-temperature phase are quadrupled. However, a smaller (half as large) orthorhombic unit cell, rotated by 45° relative to the high-symmetry ($I4/mmm$) cell, and its 90° twin, are adequate to index all the observed reflections: $a_o \approx 2\sqrt{2}a_t$, $b_o \approx \sqrt{2}a_t$, and $c_o = c_t$ ($a_t$ and $c_t$ are the tetragonal lattice constants). This orthorhombic unit cell is consistent with the one used to describe the charge-ordered phases of the perovskite La$_{0.50}$Ca$_{0.50}$MnO$_3$ [17] and the bi-layer material LaSr$_2$Mn$_2$O$_7$ [16]. However, it is different from the cell proposed by Sternlieb et al. for La$_{0.50}$Sr$_{1.50}$MnO$_4$ [14].

After an extensive survey of reciprocal space we are forced to conclude that the low-temperature structural symmetry is lower than previously reported. It is no higher than the orthorhombic extinction class $A - - -$. A common characteristic of these structures is that they contain three unique Mn sites in a $1 : 1 : 2$ ratio and that equivalent Mn sites are located as far apart from each other as possible. Since some of the quarter-wave peaks are very intense (up to ~1% of the intensity of the high-symmetry peaks, see Fig. 1) and are visible in neutron as well as in non-resonant x-ray scattering, the predominant contribution to the intensity of these peaks must come from a structural distortion and not from charge or orbital ordering on the Mn sites. These $h$-odd reflections are, however, heavily suppressed along $(h, 0, 0)_o$, implying that the structural distortions are not isotropic, but mostly orthogonal to the modulation direction $h$. Such a structural distortion is probably a shear-type distortion of the Mn-O octahedra (or a Jahn-Teller distortion) similar to the one proposed for La$_{0.50}$Ca$_{0.50}$MnO$_3$ [17] and LaSr$_2$Mn$_2$O$_7$ [16], rather than a breathing-type distortion of the oxygen octahedra as proposed in Ref. [1]. In light of this, we note that the resonant scattering signal at the quarter-wave positions, observed by Murakami et al. [13] for $x = \frac{1}{2}$, either could be ascribed to orbital ordering or to the charge asymmetry around the Mn ions associated with the structural distortion reported here [14]. To fully characterize the low-temperature distortion and the role charge and orbital order play in manganites, comprehensive and accurate high-resolution crystallography will be necessary.

The nature of the distortion can be more clearly identified by studying the effects of varying the $e_g$ electron concentration $n_e = 1 - x$. We observed superlattice peaks in all samples with $x > 0.40$, up to $x = 0.67$, the highest value investigated (see Fig. 2). For $x > 0.50$, the superlattice modulation vector changes linearly with $n_e$, as shown in Fig. 3(a). For $x = 0.50$, the superlattice modulation doubles the high-temperature structure (along the tetragonal base diagonal), and for $x = 0.67$, it triples it. This linear dependence of the wave vector is similar to that observed in La$_{1-x}$Ca$_x$MnO$_3$ for $x > 0.5$ [7] and, in particular, at $x = \frac{2}{3}$ [8, 17, 18, 19]. While at $x = \frac{1}{2}$ and $x = \frac{4}{5}$ commensurate wavevectors are observed, the ordering is best understood, at all doping levels $\frac{1}{2} \leq x \leq \frac{4}{5}$, as a modulation whose period only is a function of $n_e$. Because the superlattice modulation is directly correlated with $n_e$, it is likely that the structural phase transition

![FIG. 1: X-ray diffraction scans of La$_{0.50}$Sr$_{1.50}$MnO$_4$ in the low-temperature phase ($T = 7$K) along (a) $(h, 0, 0)_o$ and (b) $(h, 4, 0)_o$ ("o" indicates the orthorhombic unit cell). The peaks at $h = 8, 12, 16$ and $20$ are present in the high-temperature phase. The superlattice peaks at odd-integer values of $h$ are strongly suppressed along $(h, 0, 0)_o$. Note the logarithmic intensity scale.](image-url)
is driven by the ordering of the \( e_g \) electrons.

Second and third diffraction harmonics, much weaker than the primary (labeled as 2, 3 and 1 in Fig. 2), are visible at \((\pm 2\epsilon, 0, 0)\) and \((\pm 3\epsilon, 0, 0)\). The relative weakness of the higher harmonics suggests that the structural distortion is essentially sinusoidal [20]. The widths of the superlattice peaks are comparable to those of the high-symmetry peaks which implies that the low-temperature phase exhibits long-range order.

The nearly sinusoidal structural distortion, together with the linear variation of the modulation wavevector with doping, precludes any model in which the \( e_g \) electron order is too closely linked to the underlying cationic lattice, such as the bi-stripe model of Ref.[8] or the discommensurate-stripe model proposed for the single-layer nickelates [21]. A better description is given by a nearly sinusoidal structural distortion, probably associated with a charge-density wave. The variation of the charge density, with equivalent Mn sites located as far apart as possible, is similar to the “Wigner-crystal” arrangement of the \( e_g \) electrons proposed for \( \text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3 \) [17].

A \( 2\theta \) rotation of the modulation direction with respect to the high-temperature lattice was found from electron diffraction of \( \text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3 \) [19]. We did not observe any rotation of the structural modulation in \( \text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4 \). This is shown for \( x = 0.525 \) in Figure 3(b).

For \( x \leq 0.40 \), there exists no superlattice structure at low temperature. Rather, we observe very weak diffuse scattering similar to what we find for the disordered phase of \( x \geq 0.50 \) above the charge-ordering temperature. This diffuse intensity may arise from short-range polaron-polaron correlations similar to those reported for the paramagnetic (insulating) phase of \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) [22]. Thus, there is no long-range distortion of the high-symmetry structure for \( x \leq 0.40 \), and the \( e_g \) electrons are not ordered. Unlike the CMR manganites, \( \text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4 \) remains insulating in this region of doping [3, 10].

For \( 0.40 < x < 0.50 \), the modulation vector remains the same as for \( x = 0.50 \). However, as can be seen from Fig. 4, the intensity of the superlattice peak increases as \( x \) increases toward \( x = 0.50 \). The simplest explanation for this behavior is that the material separates into charge-ordered regions of 0.5 \( e_g \) electrons per Mn site and disordered regions of approximately 0.6 \( e_g \) electrons per Mn site. Additional support for this interpretation comes from the widths of the peaks. For \( x \geq 0.45 \), the widths of the superlattice peaks are nearly constant and comparable to the widths of the high-symmetry peaks. However, for \( x < 0.45 \), the superlattice peak widths are ten to twenty times broader and the peak intensities are much reduced, implying that the remaining ordered domains are of relatively small size.

In conclusion, we have used synchrotron x-ray scat-
tering to investigate the nature of the low-temperature structural distortion of La$_{1-x}$Sr$_{1+x}$MnO$_4$ and its dependence on the $e_g$ electron concentration $n_e = 1 - x$. At $x = 0.50$, our measurements indicate a shear-type structural distortion of the Mn-O octahedra. As a function of doping $x$, we found three distinct regions. For $x \geq 0.50$, the largely transverse structural distortion exhibits long-range order and the modulation vector of the distortion varies linearly with $n_e$: $\epsilon = 2n_e$. This distortion, which is similar to that found for $x = 2/3$ in La$_{1-x}$Ca$_x$MnO$_3$ [7, 13], appears to be associated with a nearly sinusoidal charge-density wave. Samples with $x \leq 0.40$ exhibit no long-range superstructural order, only diffuse scattering peaks, perhaps due to short-range polaron-polaron correlations. The intermediate region, $0.40 < x < 0.50$, is best understood as a mixture of the ordered and the disordered phases. This phase diagram is reminiscent of that of the CMR perovskite La$_{1-x}$Ca$_x$MnO$_3$. The structure of the ordered phase appears to primarily depend on $n_e$, and to be rather insensitive to the dimensionality of the lattice. Further, both the single-layer system and the CMR perovskites phase separate for $n_e > 0.5$. Nevertheless, in this regime their macroscopic low-temperature transport and magnetic properties differ dramatically.

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