Reentrant behavior of the charge and orbital ordering and antiferromagnetism in $LaSr_2Mn_2O_7$

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We have investigated the charge/orbital ordering of the 50% hole-doped bilayer manganite $LaSr_2Mn_2O_7$ by means of high-energy x-ray diffraction and also neutron diffraction on a single crystal. The temperature variation of the superlattice reflections corresponding to the propagation vector $\mathbf{k}=(-\frac{1}{4},\frac{1}{4},0)$ indicates the development of a coupled charge/orbital ordering below $T_{CO}\approx 225$ K which starts melting at about the same temperature at which antiferromagnetic ordering ($T_N\approx 170$ K), detected by neutron diffraction, sets in. The intensities of superlattice reflections become very small below about 100 K. In the more sensitive x-ray-diffraction experiment we observed a recovery in intensities of the superlattice reflections below about 50 K which become almost saturated at 9 K. This reentrant behavior of charge/orbital ordering is discussed in terms of a polaron model. We have investigated the resonant enhancement of the satellite reflection at the K absorption edge of Mn. The polarization analysis of the scattered beam showed that the resonance enhancement is of the dipolar origin.

Recently, the interplay among spin, charge, orbital, and lattice degrees of freedom in strongly correlated electron systems like transition-metal oxides has attracted considerable attention from condensed-matter physicists. The bilayer manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$, which have become the subject of much investigation due to their colossal magnetoresistance (CMR) behavior,[1–7] are potential candidates for such interplay. Because of the reduced dimensionality the physical properties of the bilayer manganites are different from those of three-dimensional manganites.[8] For example, the magnetoresistance is greatly enhanced in the bilayer manganite ($x=0.4$) although at the cost of a reduced ferromagnetic transition temperature. Since the 50% hole-doped ($x=\frac{1}{2}$) bilayer manganite $LaSr_2Mn_2O_7$ consists of formally equal amounts (50%) of Mn^{3+} and Mn^{4+} ions, one expects, in analogy with the three-dimensional manganites, both charge ordering and also the associated ordering of the orbitals.[9,10] Here we report a high-energy x-ray- and neutron-diffraction investigation of the reentrant behavior of the charge/orbital ordering in $LaSr_2Mn_2O_7$ and the possible role of two-dimensional spin correlations and magnetic ordering on it. Our results directly show strong interplay among spin, charge, orbital, and lattice degrees of freedom in $LaSr_2Mn_2O_7$ and strongly suggest that the in-plane ferromagnetic ordering causes melting of the charge/orbital order.

A thin plate-shaped single crystal of linear dimensions $4\times 4\times 0.5\,mm^3$ was used for both the high-energy x-ray- and neutron-diffraction experiments. Magnetization and electrical resistivity measurements have been made on the same crystal and have been reported.[11] For the high-energy (120 keV) x-ray experiment the crystal was mounted inside a Displex refrigerator made of Al on a four-circle diffractometer on the high-energy wiggler beam line BW5 of the HASYLAB at DESY. Resonant x-ray diffraction at the Mn *K*-edge ($E=6545$ eV) was carried out on the wiggler beam line W1 of the HASYLAB at DESY. The sample was mounted on a Displex refrigerator with Be dome. Neutron-scattering experiments were carried out on the four-circle diffractometer D10 of the Institut Laue-Langevin in Grenoble with the sample placed inside a four-circle helium-flow cryostat. A neutron beam of wavelength 2.36 Å was obtained using a PG (002) monochromator. In the high-energy x-ray and neutron experiments, absorption is negligible and the observed scattering is from the whole sample. But in the medium energy resonant x-ray experiment at the *K* absorption edge, the absorption is very large. Only a very small fraction of the crystal contributes to the scattered intensities.

In the x-ray experiment a search for superlattice reflections belonging to the fundamental 110 reflection showed very intense satellite reflections at $\mathbf{Q}=(\frac{5}{4},\frac{3}{4},0)$ and $\mathbf{Q}=(\frac{3}{4},\frac{5}{4},0)$, but not at $\mathbf{Q}=(\frac{5}{4},\frac{5}{4},0)$ and $\mathbf{Q}=(\frac{3}{4},\frac{3}{4},0)$. The propagation vector is $\mathbf{k}=(-\frac{1}{4},\frac{1}{4},0)$ and the sample seems to be an orthorhombic single domain. Figure 1(a) shows the temperature variation of the $\frac{3}{4},\frac{5}{4},0$ reflection as a function of

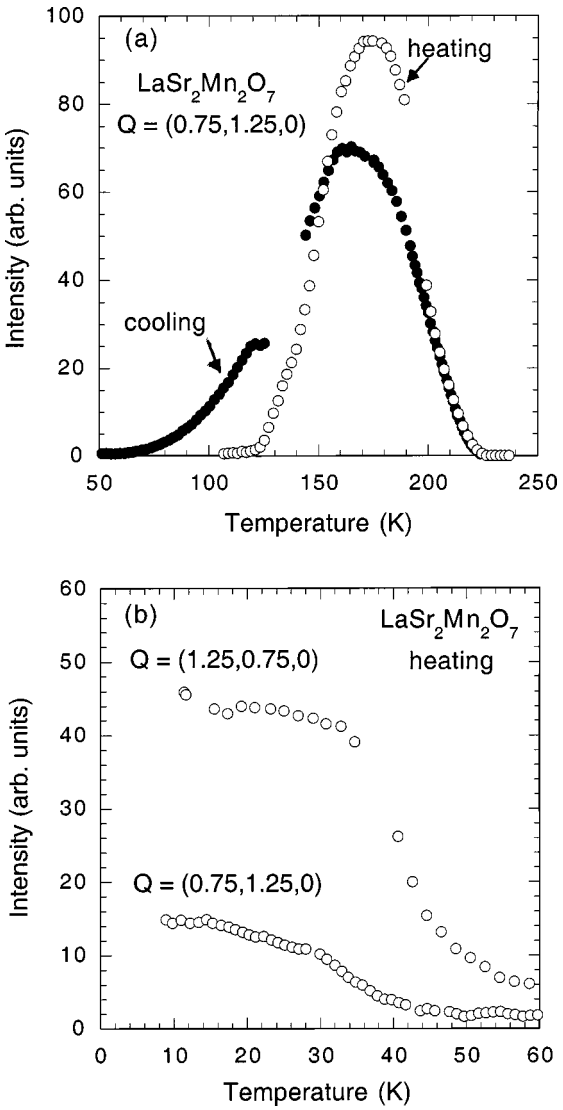

FIG. 1. (a) Temperature variation of the intensity of the $(\frac{3}{4},\frac{5}{4},0)$ superlattice reflection from $LaSr_2Mn_2O_7$ measured by x-ray diffraction with an absorber (factor$\approx$18.6). The gaps in the data points are due to the storage-ring filling. (b) Temperature variation of the intensities of $(\frac{3}{4},\frac{5}{4},0)$ and $(\frac{5}{4},\frac{3}{4},0)$ reflections (no absorber) below 60 K demonstrating their reentrant behavior.

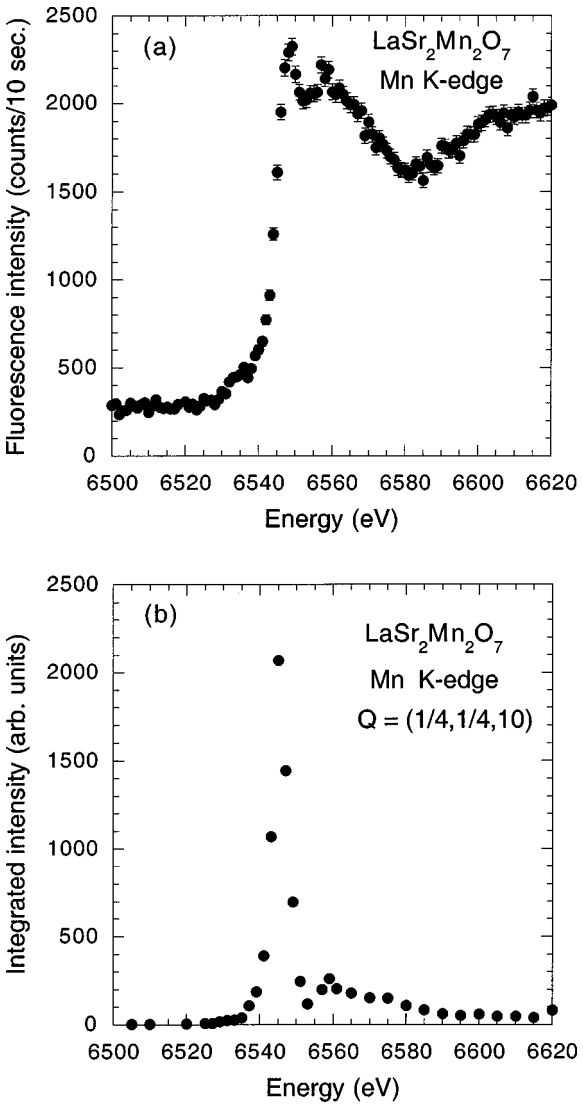

FIG. 2. (a) Total fluorescence yield from the $LaSr_2Mn_2O_7$ sample as a function of the x-ray energy. (b) The energy variation of the integrated intensity of the $\frac{1}{4},\frac{1}{4},10$ reflection.

temperature. Its intensity increases continuously below $T_{CO} \approx 225$ K. It passes through a maximum at about 160 K and then decreases and becomes very small but nonzero at about 50 K. Figure 1(a) demonstrates the existence of appreciable hysteresis at the lower boundary of this phase. Very similar behavior was observed for the $\frac{5}{4},\frac{3}{4},0$ reflection which has peak intensity three times that that of the $\frac{3}{4},\frac{5}{4},0$ reflection. It is to be noted that these reflections are very strong. These observations are in agreement with those of Kimura *et al.*,[10] but the present data are far more precise. Kimura *et al.*[10] stated that the intensities of the superlattice reflections become zero below 50–100 K. In our experiment these intensities were observed to remain nonzero at lower temperatures. In fact, these intensities start growing again below about 50 K to saturate at about 9 K, the lowest temperature obtained during the experiment. Figure 1(b) shows this low-temperature reentrant behavior. The saturated intensity at 9 K is lower by a factor of about 128 than the peak intensity at 175 K. In agreement with Ref. 10 we interpret the satellite reflections as being due to the charge ordering of the Mn^{3+} and Mn^{4+} ions coupled with staggered $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbital ordering of the Mn^{3+}.

We have investigated the resonant enhancement of the satellite reflections at the Mn *K* edge. Figure 2(a) shows the total fluorescence yield from the $LaSr_2Mn_2O_7$ sample as a function of the x-ray energy. Because of the geometrical restriction with the absorbing medium energy x-rays we could not measure the satellite corresponding to the 110 main reflection. Instead we measured the satellite $\frac{1}{4},\frac{1}{4},10$ reflection. Figure 2(b) shows the energy variation of the integrated intensity of the $\frac{1}{4},\frac{1}{4},10$ reflection. Due to the large absorption with the medium energy x-rays, the intensity of the satellite reflection is very small below the *K* absorption edge of Mn. But as the energy was tuned close to the *K* absorption edge a very large enhancement of the intensity was observed. The energy variation of the intensity shows a peak at the absorption edge ($E = 6545$ eV) and then decreases above the edge. However, a broad peak is observed at higher energy (E

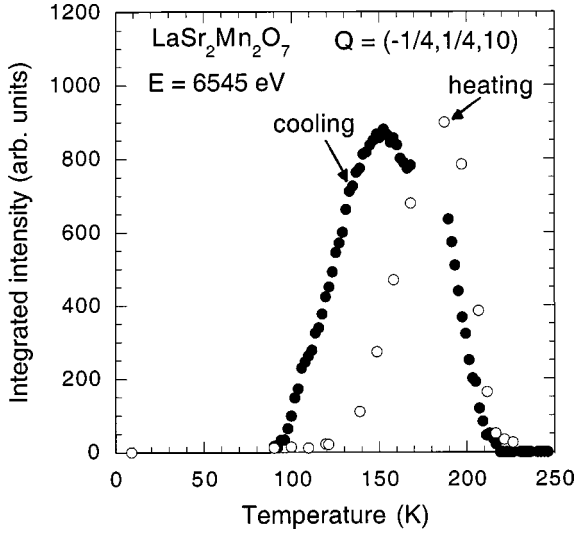

FIG. 3. Temperature dependence of the integrated intensity of the $\frac{1}{4},\frac{1}{4},10$ satellite reflection.

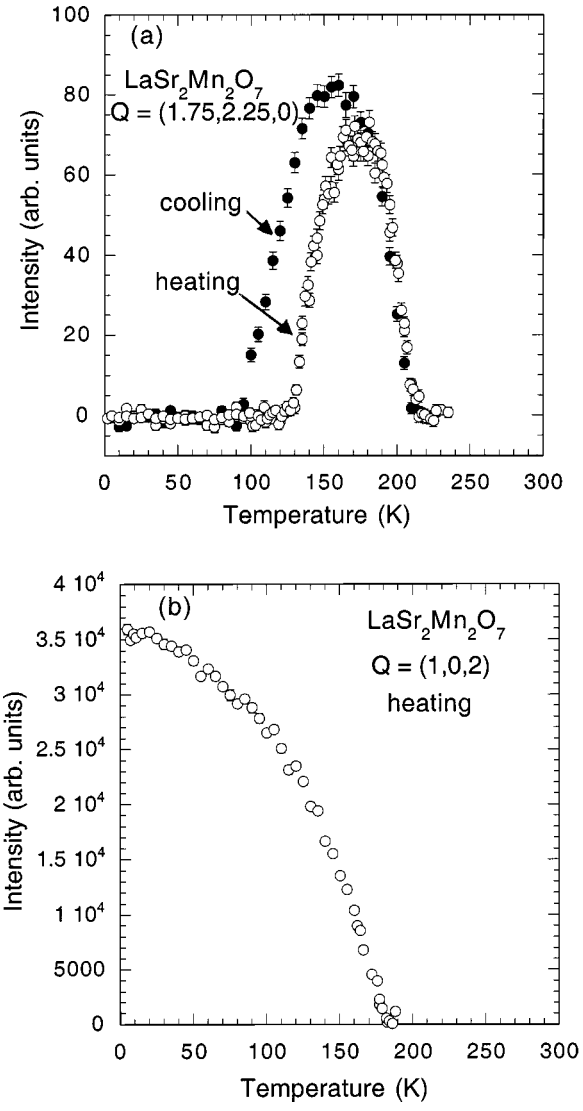

FIG. 4. (a) Temperature variation of the intensity of the $(\frac{7}{4},\frac{9}{4},0)$ reflection from $LaSr_2Mn_2O_7$ measured by neutron diffraction. (b) The temperature variation of the the magnetic 102 reflection.

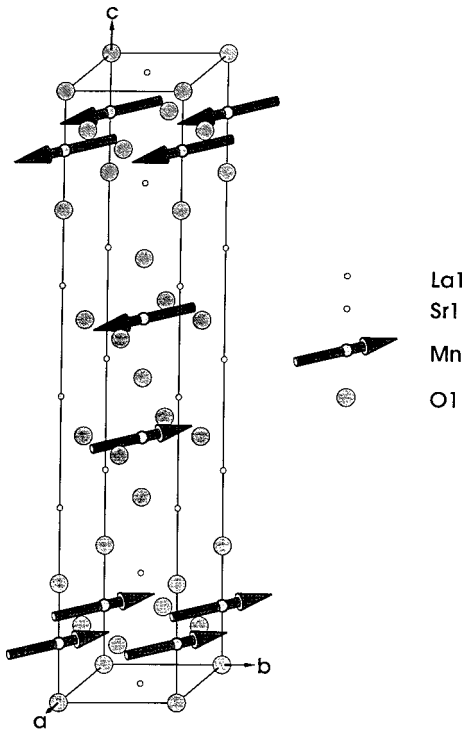

FIG. 5. Schematic representation of the antiferromagnetic structure of $LaSr_2Mn_2O_7$.

$=6560$ eV). We interpret the broad peak at the higher energy due to the transition to the *p* band. We have carried out polarization analysis of the scattered intensity at $E=6545$ eV and found that the polarization is rotated by $\pi/2$. We observe no intensity in the $(\sigma-\sigma)$ channel whereas a large intensity was observed in the $(\sigma-\pi)$ channel. This shows that the transition at the absorption edge is of the dipolar type. We also measured the intensity in both $(\sigma-\sigma)$ and $(\sigma-\pi)$ channel at $E=6434$ eV. At this energy we see smaller but easily measurable intensity in the $(\sigma-\sigma)$ channel and of course more intensity in the $(\sigma-\pi)$ channel. This may be partly due to the admixture of the quadrupole transition, but since the nonresonant scattering contributes to the $(\sigma-\sigma)$ channel, no definite conclusion can be made about the nature of the transition at this energy. We have not carried out polarization analysis at the broad peak presumably due to the transition to the *p* band. We have measured the temperature dependence of the intensity of the $\frac{1}{4},\frac{1}{4},10$ satellite reflection shown in Fig. 3. The temperature dependence is very similar to that observed for the $\frac{3}{4},\frac{5}{4},0$ satellite reflection [Fig. 1(a)].

In the neutron-diffraction experiment we also readily detected superlattice reflections corresponding to the propagation vector $\mathbf{k}=(-\frac{1}{4},\frac{1}{4},0)$ below $T_{CO}\approx 210$ K. Figure 4(a) shows the temperature variation of the intensity of the $\frac{7}{4},\frac{9}{4},0$ superlattice reflection in both heating and cooling cycles which resembles closely the variation measured using x-rays (Fig. 1). However, the increase in intensity observed at lower temperature in the x-ray experiment could not be measured by neutron diffraction due to its relatively small value. The superlattice intensity measured in the neutron-diffraction experiment is due to the structural distortion associated with the charge/orbital ordering. Only resonant x-ray diffraction can probe the charge/orbital ordering directly.

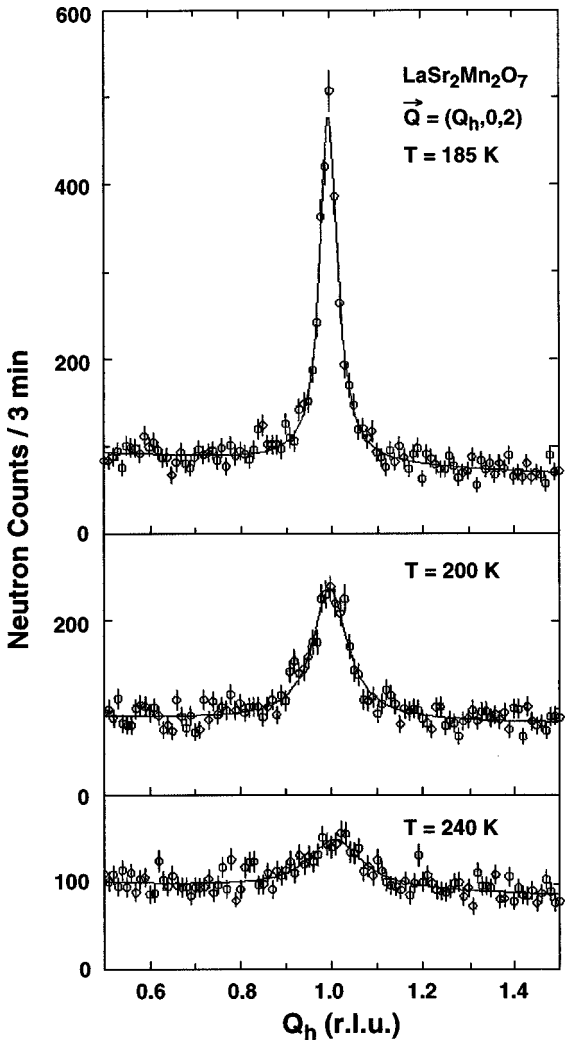

FIG. 6. Q_h scans perpendicular to the $[10l]$ rod at $l=2$ from $LaSr_2Mn_2O_7$ at several temperatures. The continuous curves are the results of least-squares fits with Lorentzian profiles.

A search for magnetic reflections in the neutron experiment revealed their presence at reciprocal lattice points $h+k+l=2n+1$ [the propagation vector $\mathbf{k}=(1,0,0)$] at which the nuclear Bragg peaks are absent due to the body centering of the lattice ($I4/mmm$). We measured the intensities of 41 nuclear and 36 magnetic symmetry independent reflections at $T=5$ K. Refining the antiferromagnetic structure model (Fig. 5) against the measured magnetic intensities gave a Mn magnetic moment $2.82\pm0.05\mu_B$ with agreement factors $R=9\%$ and $\chi^2=3.1$. The magnetic structure of the bilayer is A type, i.e., with the ferromagnetic layers stacked antiferromagnetically. These results are in agreement with that of Ref. 7. The interbilayer stacking is ferromagnetic. Figure 4(b) shows the temperature variation of the magnetic 102 reflection measured by neutron diffraction. This reflection first appears below $T_N\approx170$ K. Its intensity increases continuously with decreasing temperature and becomes saturated at low temperature. Note that the temperature $T\approx170$ K at which the intensities of the superlattice reflections corresponding to the charge/orbital ordering start decreasing coincides with the magnetic ordering temperature $T_N\approx170$ K.

We have investigated the diffuse magnetic scattering by

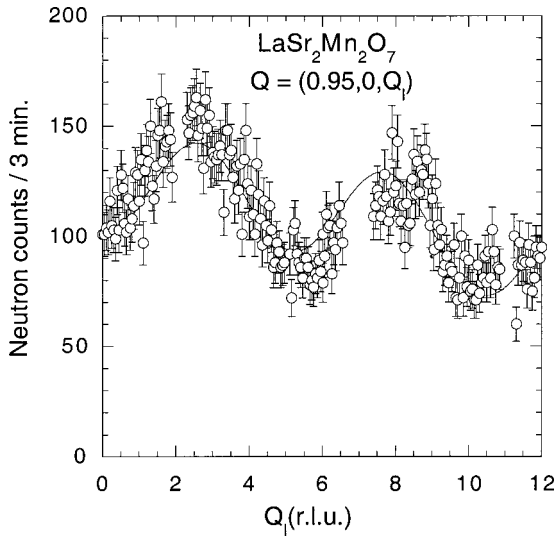

FIG. 7. Intensity of the diffuse scattering from $LaSr_2Mn_2O_7$ along $\mathbf{Q}=(0.95,0,l)$ (parallel to the rod) at $T=185$ K. The continuous curve is the result of the least-squares fit of the diffuse intensity to Eq. (1). The gaps in the data points are due to Bragg contaminations which have been removed.

performing Q scans parallel to a^* through $\mathbf{Q}=(1,0,2)$ and $\mathbf{Q}=(1,0,4)$ and also parallel to c^* along $(0.95, 0, l)$. We observed two-dimensional rodlike magnetic scattering along c^* through the magnetic reflections. Figure 6 shows Q scans perpendicular to the $(10l)$ rod at $l=2$ at several temperatures below and above T_N. The diffuse scattering is still observed at 295 K which is about $1.7\times T_N$. The in-plane correlation length at different temperatures has been determined from the half-widths of scans perpendicular to the rod. It increases continuously with decreasing temperature from about 7 Å at 295 K to about 110 Å close to T_N. Due to the large separation between successive bilayers, the modulation of the diffuse scattering along the rod is determined by the correlations between Mn spins belonging to the two layers of the bilayer. The energy-integrated magnetic neutron-scattering cross section for the wave-vector transfer Q is proportional to

$$S(\mathbf{Q})\propto f(Q)^2(1\pm\cos 4\pi 2zl), \tag{1}$$

where $f(Q)$ is the form factor of the Mn atom, $(0, 0, z)$ is the position of the Mn atom in the unit cell, and the plus or minus signs correspond to ferro- or antiferromagnetic correlations, respectively, between the two planes of the bilayer. Since the two ferromagnetic layers of a single bilayer couple antiferromagnetically in the ordered structure, we expect antiferromagnetic correlations between the two planes of the bilayer above T_N and therefore the minus sign is relevant in the present case. The oscillation of the intensity along the rod should therefore have the opposite phase to that observed in $La_{1.2}Sr_{1.8}Mn_2O_7$,[6,12] as is indeed the case. From our structural refinement of $LaSr_2Mn_2O_7$ with neutron-diffraction data we determined $z=0.0969\pm0.0004$. So the diffuse intensity is expected to show a minimum at $l=0$ and a maximum at $l=2.58$. Figure 7 shows that there is a very good fit between

the diffuse-scattering intensity as a function of Q_l parallel to the rod along the $\mathbf{Q}=(0.95,0,l)$ direction at $T=200$ K and Eq. (1) with $z=0.0969$.

Our present investigation strongly suggests the development of CE-type charge/orbital ordering in $LaSr_2Mn_2O_7$ below $T_{CO}\approx 225$ K as predicted by Goodenough[13] decades ago. Only the associated CE-type magnetic ordering is not observed. The melting of the charge/orbital order at about 100 K can be understood qualitatively. Although the net magnetic ordering at $T_N\approx 170$ K is antiferromagnetic, the ordering within each *a*-*b* plane is ferromagnetic. It is likely that onset of ferromagnetic order in the individual *a*-*b* planes causes melting of the charge/orbital ordering. Also the antiferromagnetic ordering (Fig. 3) is not consistent with the CE-type charge ordering. However, this does not explain the reentrant behavior of the charge/orbital ordering at low temperature.

Based on a two-dimensional extended Hubbard model with electron-phonon interaction, Yuan and Thalmeier[14] have studied recently the effect of small polaron formation on the charge-ordering (CO) transition. For fully ferromagnetically ordered spins the appearance, collapse, and reappearance of the CO state with decreasing temperature is caused by the temperature dependence of the polaron bandwidth. In this theory charge ordering corresponding to the propagation vector $\mathbf{k}=(\frac{1}{2},\frac{1}{2},0)$ has been considered but the possibility of orbital ordering has not been taken into account. However, in our present investigations, the satellite reflections have been observed corresponding to the propagation vector $\mathbf{k}=(-\frac{1}{4},\frac{1}{4},0)$ only. One can of course think of a model of charge ordering only which would produce superlattice reflections corresponding to the propagation vector $\mathbf{k}=(-\frac{1}{4},\frac{1}{4},0)$. One has to consider a row of Mn^{3+}-Mn^{3+}-Mn^{4+}-Mn^{4+} along *a* and stacking them along *b* such that similar rows are also obtained along *b*. This is a sort of narrow stripe ordering. Whether such a charge ordering is energetically favorable and can give rise to reentrant behavior can only be decided from similar calculations to those of Ref. 14. But the charge ordering of the Mn^{3+} and Mn^{4+} ions coupled with staggered $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbital ordering of the Mn^{3+} ions is consistent with the experimental observations and should be incorporated in the polaron model of Ref. 14.

In conclusion, our present investigations demonstrate the complex interplay among the spin, charge, orbital, and lattice degrees of freedom in the 50% hole-doped quasi-two-dimensional bilayer manganite $LaSr_2Mn_2O_7$. Reentrant behavior of the charge/orbital ordering is observed. We have shown that the two ferromagnetic planes of the bilayer are antiferromagnetically stacked in the ordered phase below $T_N\approx 170$ K and antiferromagnetic correlation between them persists above T_N.

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