Electronically smecticlike liquid-crystal phase in a nearly half-doped manganite

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We use neutron scattering to study the spin and charge-orbital ordering (CO-OO) in the nearly half-doped perovskite manganite $Pr_{0.55}(Ca_{0.8}Sr_{0.2})_{0.45}MnO_3$ (PCSMO). On cooling from room temperature, PCSMO first enters into a CO-OO state below T_{CO} and then becomes a CE-type long-range ordered antiferromagnet below T_N. At temperatures above T_N but below T_{CO} ($T_N<T<T_{CO}$), the spins in PCSMO form highly anisotropic smectic liquid-crystal-like texture with ferromagnetic (FM) quasi-long-range ordered one-dimensional zigzag chains weakly coupled antiferromagnetically. Such a magnetic smecticlike phase results directly from the spin-orbit interaction and demonstrates the presence of textured "electronic soft" phases in doped Mott insulators.

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The manganese oxides with general composition $R_{1-x}A_xMnO_3$ (where R and A are rare- and alkaline-earth ions) have been actively investigated over the past decades because of the colossal magnetoresistance (CMR) effect observed around $x=0.30$. The fascinating properties of these materials have been attributed to the electronic complexity arising from the strong competition between charge, orbital, lattice, and magnetic degrees of freedom.[1,2] Of particular interest is the case of the half-doped ($x=0.5$) manganites. When cooling from room temperature, they form a structure that has been described as a "charge and orbital ordered" (CO-OO) state, where Mn^{3+} and Mn^{4+} ions are arranged alternatively in the form of checkerboard-like order below T_{CO}.[3,4] On further cooling, the spins order into the CE-type magnetic structure below T_N [Fig. 1(a)]. In the intermediate temperature region above T_N but below T_{CO} ($T_N<T<T_{CO}$), there is a coexistence of incommensurate and inhomogeneous magnetic and CO-OO ordered states.[5] The nature of such coexistence is still unclear and it has been recently suggested that it is related to the emergence of new electronic soft phases.[1,6] In this Brief Report, we present comprehensive neutron scattering studies on a nearly half-doped perovskite manganite $Pr_{0.55}(Ca_{0.8}Sr_{0.2})_{0.45}MnO_3$ (PCSMO) focusing in the purported "electronically soft" phase regime of $T_N<T<T_{CO}$. We choose PCSMO because this material has well separated CO-OO and AF transitions ideally suited for our investigation.[7] While the CO-OO fluctuations in PCSMO are spatially isotropic as expected, the AF spin fluctuations are highly anisotropic and indicative of the formation of quasi-long-range FM ordered 1D spin chains that are weakly coupled antiferromagnetically. The anisotropic and low-dimensional character of the spin fluctuations is counterintuitive in a conventional paramagnetic state, as PCSMO is essentially cubic. We argue that these features are due to the anisotropy of the short-range Double Exchange interactions as proposed by Van den Brink *et al.* and Solovyev and Terakura,[8,9] and that the complex coexistence of the magnetic and charge-orbital fluctuations in this regime arises from the magnetic exchange and the orbital degeneracy of the Mn ions. Our results highlight the role of the orbital physics in determining the electronic properties of the half-doped manganites and support the idea that the charge-orbital and magnetic fluctuations have the same magnetic origin. The observed highly anisotropic spin texture is reminiscent of the smectic phases[10] predicted in the doped Mott insulators[11] and is the first example of the textured "electronically soft" phases in the CMR manganites.[6]

We grew a single crystal of PCSMO using the floating zone method.[7] PCSMO has the *Pbnm* symmetry in the low-temperature orthorhombic phase ($a\approx b\approx 3.85$ Å and $c\approx 3.79$ Å below T_{CO}), slightly distorted from the cubic lattice. The sample is naturally twinned due to the small orthorhombicity, the twinning domains are 90° rotated with respect to each other in the scattering plane. For simplicity, we use a pseudocubic unit cell with lattice parameters of $a\approx b\approx c\approx 3.84$ Å, and all the wave vectors below refer to the cubic notation. The momentum transfers $\vec{q}=(q_x,q_y,q_z)$ in units of $Å^{-1}$ are at positions $(h,k,l)=(q_xa/2\pi,q_ya/2\pi,q_za/2\pi)$ in reciprocal lattice units (rlu). The sample was aligned to allow the wavevector in the form of $(h,k,0)$ accessible in the horizontal scattering plane. Our neutron scattering experiments were carried out using thermal neutron triple-axis spectrometers at the High-Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory, the NIST Center for Neutron Research, and the JRR-3 reactor JAERI, Tokai, Japan. The neutron energy was fixed at $E=14.7$ meV using pyrolytic graphite crystals as monochromators, analyzers and filters.

Upon cooling PCSMO undergoes a series of transitions. It

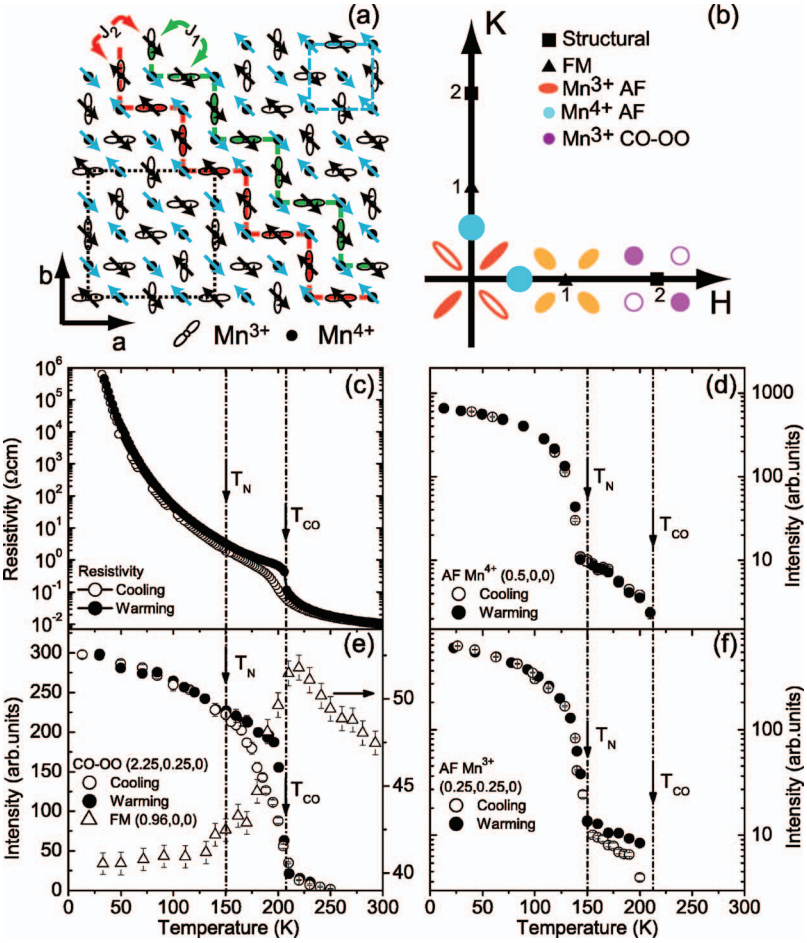

FIG. 1. (Color) Panel (a) shows schematic diagram of the CE-type structure in the nearly half doped perovskite manganites in the cubic setting. The zigzag chains formed by alternating Mn^{3+} and Mn^{4+} spins are coupled antiferromagnetically, the coupling within the chain is ferromagnetic. The short-dashed line denotes the periodicity of the Mn^{3+} orbital and magnetic unit cell, long-dashed line shows the Mn^{4+} magnetic unit cell. Panel (b) depicts the corresponding superlattice peaks in the reciprocal space (solid symbols). Open symbols indicate superlattice peaks that are forbidden in a single-domain crystal but are observed because of twining. Bottom: Temperature dependence of (c) resistivity; (d) AF peak intensity from (0.5,0,0); (e) CO-OO peak intensity from (2.25,0.25,0) and FM short-range fluctuations from (0.96,0,0); and (f) AF peak intensity from (0.25,0.25,0). In panels (c)–(f) open and solid symbols represent cooling and warming, respectively.

first enters the CO-OO state below $T_{CO} \sim 210$ K and becomes a long-range antiferromagnet below $T_N \sim 150$ K with a CE-type spin arrangement.[3] Neutron diffraction is not sensitive to the ordering of orbitals but it can measure the superlattices associated with the lattice distortions caused by such order. In a twinned crystal, the characteristic propagation wavevectors of the CO-OO structure are $\vec{q}=(1/4,1/4,0)$ (which is also the propagation wave vector for the network of Mn^{3+} spins), and $\vec{q}=(1/2,0,0)$ is the propagation wave vector for the Mn^{4+} spins network.[12] Experimentally the intensity of the scattering at a wave vector $\vec{Q}=(\vec{q}+\vec{\tau})$, where $\vec{\tau}$ is a vector of the reciprocal lattice and $\vec{q}$ is the propagation wave vector, provides a measurement of the order parameter for such structure. Since the neutron scattering cross section is proportional to the square of the magnetic form factor, which decreases rapidly at large scattering wavevectors, one can choose "large" wave vectors $\vec{Q}$ to probe the CO-OO and "small" $\vec{Q}$'s to probe the magnetic ordering. In our neutron diffraction experiments, we used $\vec{Q}=(2.25,0.25,0)$, (0.25,0.25,0) and (0.96,0,0) to measure the CO-OO, AF and FM fluctuations, respectively. We also used $\vec{Q}=(0.5,0,0)$ to probe the AF fluctuations related to the Mn^{4+} spins [Fig. 1(b)].

Figures 1(c)–1(f) show the temperature dependence of the resistivity[7] and the peak intensities associated with AF, FM, CO-OO fluctuations as the sample is cooled in zero magnetic

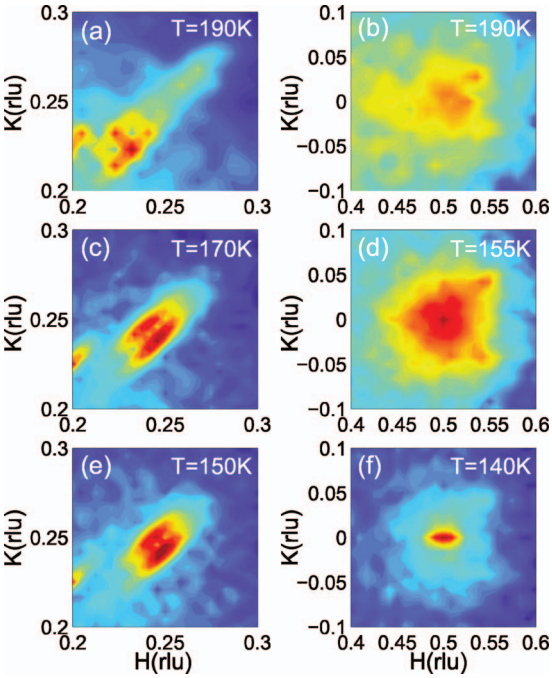

FIG. 2. (Color) Panels (a), (c), (e) show mesh scans around the AF Bragg peaks (0.25,0.25,0) at $T=190$, 170, and 150 K. Panels (b), (d), (f) show mesh scans around (0.5,0,0) at $T=190$, 155, and 140 K.

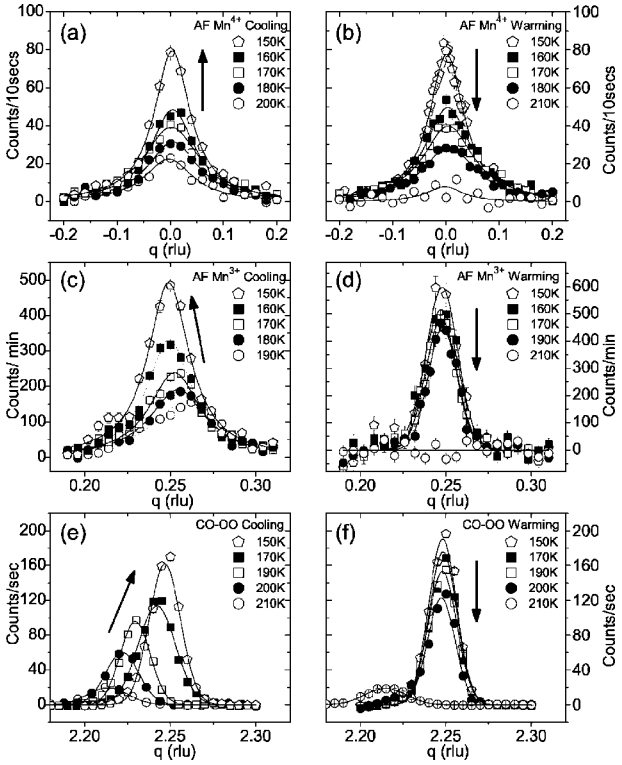

FIG. 3. Representative wave vector scans of the AF component near (0.5,0,0) on (a) cooling and (b) warming; of the AF component near (0.25,0.25,0) on (c) cooling and (d) warming; and CO-OO components near (2.25,0.25,0) on (e) cooling and (f) warming. The data shown in (c) and (d) have sloping background subtracted.

field. The resistivity exhibits insulating behavior at all temperatures with a distinct feature around $T_{CO}=210$ K in the ρ-T curve. The hysteresis in the resistivity near T_{CO} is accompanied by a first-order structural transition from pseudocubic to orthorhombic phase causing a small splitting of the (2,0,0) lattice peak. The CO-OO peak intensity in Fig. 1(e) also shows an abrupt change near T_{CO} with strong hysteresis. The clear correlation between the resistivity and the CO-OO peak intensity indicates that the transport properties of these materials are mostly governed by the localization and delocalization of charge carries.[13,14] PCSMO does not exhibit long-range FM order in zero magnetic field but develops short-range FM spin fluctuations above T_N. These fluctuations increase with decreasing temperature, peak at T_{CO}, and are greatly suppressed at low temperatures [Fig. 1(e)]. The most interesting findings come from the temperature dependence of the AF intensities associated with the Mn^{3+} and Mn^{4+} spin fluctuations. As shown in Figs. 1(d) and 1(f), weak AF spin fluctuations appear just below T_{CO} and increase gradually with cooling. An abrupt change takes place below $T_N \sim 150$ K, where the sample enters the long-range AF ordered pseudo-CE phase.

To probe the characteristics of AF fluctuations in $T_N < T < T_{CO}$, we performed mesh scans in reciprocal space near the $\vec{Q}=(0.25,0.25,0)$ and $\vec{Q}=(0.5,0,0)$ AF ordering positions corresponding to the Mn^{3+} and Mn^{4+} spin fluctuations respectively. Panels (a), (c), and (e) of Fig. 2 show the evolution of the AF ordering associated with the Mn^{3+} fluctuations at $T=190$, 170, and 150 K. These AF fluctuations are clearly anisotropic, with the profile in the longitudinal [1,1,0] direction being considerably broader than that in the transverse $[-1,1,0]$ direction. This indicates that the correlation of spins in the [1,1,0] direction is much weaker than along $[-1,1,0]$. The corresponding evolution of the AF ordering associated with the Mn^{4+} fluctuations, on the other hand, remains isotropic at all temperatures as illustrated in panels (b), (d), and (f). These observations are consistent with the formation of weakly antiferromagnetically coupled, quasi-long-range FM ordered 1D Mn^{3+} spins in an isotropic Mn^{4+} spins background. While our neutron scattering measurements allow us to probe the networks of Mn^{3+} and Mn^{4+} spins separately, we cannot overlook the fact that these two types of spins interact strongly via the double exchange (DE) process. This mechanism allows electron hopping between neighboring Mn^{3+} and Mn^{4+} if they have parallel spins and leads to the formation of the zigzag alternating Mn^{3+}/Mn^{4+} chains shown in Fig. 1(a).[8]

Figure 3 shows the profiles of the scattering from AF and CO-OO fluctuations at representative temperatures on cooling and warming. Broad AF fluctuation peaks can be measured below T_{CO} (there is no measurable signal above this temperature). The peak associated with the Mn^{4+} AF fluctuations is commensurate with $\vec{q}_c=(1/2,0,0)$ at all temperatures on cooling and on warming [Figs. 3(a) and 3(b)] with no hysteresis. The peaks associated with the Mn^{3+} AF and CO-OO fluctuations, on the other hand, are history dependent. They are incommensurate at T_{CO}, shift toward $\vec{q}_c=(1/4,1/4,0)$ upon cooling, and lock into this commensurate position at T_N. Upon warming to T_{CO} the scattering remains commensurate as summarized in Figs. 4(a) and 4(c). Figure 4(b) shows the measured longitudinal and transverse widths of the scattering associated with Mn^{3+} AF fluctua-

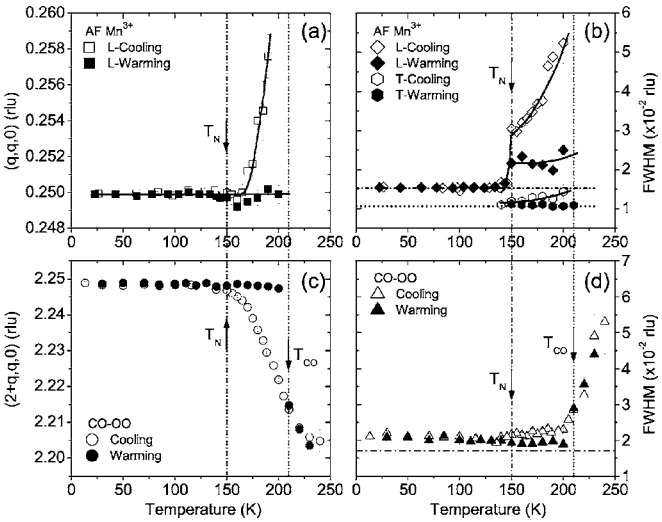

FIG. 4. Temperature dependence of (a) propagation wave vector and (b) FWHM for Mn^{3+} AF ordering. The corresponding T dependence of (c) propagation wave vector and (d) FWHM for CO-OO. "L" refers to the [1 1 0] direction and reflects the interchain coupling. "T" refers to the [−1 1 0] direction and is associated with the intrachain coupling. Dashed lines indicate the instrumental resolution.

tions. These linewidths decrease upon cooling and the AF scattering becomes isotropic and resolution limited when $T \leqslant T_N$. From these linewidths we calculated the correlation lengths[15] along the 1D FM spin chains (intrachain coupling) and perpendicular to these (interchain coupling). The intrachain correlation length ξ_T is around 200 Å at 190 K and is only weakly temperature dependent. The interchain correlation correlation length ξ_L increases from 33 Å at $T = 190$ K to 75 Å on cooling to 150 K. This result indicates that the quasi long-range FM 1D spin chains are only weakly coupled below T_{CO}, and that the interchain coupling becomes stronger as T_N is approached. This highly anisotropic spin texture is reminiscent of the electronically liquid-crystal-like smectic phases proposed in the doped Mott insulators.[11] The scattering from the CO-OO fluctuations is isotropic[16] with linewidths that decrease upon cooling. These linewidths, however, remain greater than the instrumental resolution [Fig. 4(d)], even at the lowest temperature.

The differences among the behaviors described above suggest that the interplay between the AF and CO-OO fluctuations in the paramagnetic phase of PCSMO ($T_N \leqslant T \leqslant T_{CO}$) is more complex than expected. The coexistence of AF and CO-OO fluctuations suggests a strong correlation between them. The conventional wisdom is that the CO-OO should occur at a higher temperature, of the order of the covalent bonding energy as originally proposed by Goodenough,[4] independent of the magnetic interactions. However, Goodenough's conjecture of ordered Mn^{3+} and Mn^{4+} ions may not be accurate as the actual charge disproportionality of the Mn atoms is much smaller than unity.[17–19] The interplay of Mn charges, orbitals and spins would then be reduced to the competition of the kinetic energy of the electrons and the magnetic exchange interactions.[8,9] This competition combined with the orbital degeneracy should lead to the experimentally observed CO-OO and drive the formation of 1D ferromagnetic zigzag chains that are first loosely correlated and then lock in the magnetic CE structure of Fig. 1(a) below T_N. The idea that the CO-OO is independent of the magnetic interactions seems to be far from true, and it is even possible that the CO-OO is driven by the symmetry breaking caused by the magnetic texture.[9,20] It is remarkable that despite the reported small charge disproportionality between the Mn ions[17–19] there are dramatically distinctive behaviors of the Mn ions located at the Mn^{3+} and Mn^{4+} sites as illustrated in Fig. 2. The highly anisotropic and low-dimensional behavior of the Mn^{3+} ions in this basically cubic material highlights the role of the orbitals in the formation of the 1D spin chains in this regime. Recently, Dagotto[1] and Milward *et al.*[6] have discussed the complex electronic behaviors deriving from the strong energy competitions in the CMR manganites. These authors proposed the presence of textured electronically soft phases with incommensurate, inhomogeneous, and mixed orders in the paramagnetic state. The observed smectic liquid-crystal-like weakly coupled, 1D FM zigzag chains in PCSMO confirm the presence of the sought after textured electronic soft phase predicted in the manganites[1,6] and cuprates.[11]

In summary, we have studied the CO-OO and magnetic ordering in the nearly half-doped manganite PCSMO using neutron scattering. In the paramagnetic state $T_N < T < T_{CO}$, we find the coexistence of FM, CO-OO and AF fluctuations. This coexistence arises from the competition between the kinetic energy and the magnetic exchange, and from the orbital degeneracy of the Mn ions. While the CO-OO and AF fluctuations are strongly correlated in this temperature region, they also exhibit distinctive behaviors. Remarkably, the AF short-range spin fluctuations of the Mn^{3+} spins are highly anisotropic and exhibit anisotropic smecticlike spin texture, consistent with the presence of an electronically soft phase as recently proposed in the literature.

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