What Coexists with the Ferromagnetic Metallic Phase in Manganites?

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Abstract

Colossal magnetoresistance, whereby the application of a magnetic field reduces the resistivity of a manganite by orders of magnitude, is generally believed to occur because of coexisting phases. Development of a complete theory to explain the phenomenon requires that the exact nature of these phases be known. We used resonant elastic soft x-ray scattering to examine the superlattice order that exists in $La_{0.35}Pr_{0.275}Ca_{0.375}MnO_3$ above and below the Curie temperature. By measuring the resonance profile of the scattered x-rays at different values of q, we disentangle the contributions of orbital order and antiferromagnetism to the scattering signal above the Curie temperature. Below the Curie temperature, we see no signal from orbital order, and only antiferromagnetism coexists with the dominant ferromagnetic metallic phase.

Mixed-valence perovskite manganites are well-known for exhibiting colossal magnetoresistance (CMR): the application of a magnetic field of a few tesla can drastically reduce the resistivity of a manganite sample [1]. It is generally agreed that CMR arises in part from the coexistence and competition between insulating and metallic ground states, although the exact nature of their interplay is not clear. The insulating phase is generally a combination of charge order (CO), orbital order (OO), and antiferromagnetism (AF), which constitute superlattice (SL) order with a period of multiple lattice constants. The other phase is ferromagnetic metallic (FM). Applying a magnetic field to a manganite in the CO/OO/AF state increases its conductivity by orders of magnitude [2], and it is widely accepted that the effect of the field is to suppress the CO/OO/AF and replace it with the FM state [1]. The vastly different types of order present in manganites have similar energy scales, so a seemingly inconsequential difference between the composition of two materials is enough to push the materials towards different ground states. Even within a single material, multiple phases coexist, in a phenomenon known as phase separation, which plays a crucial role in CMR [1]. In particular, x-ray [3], electron [4–6] and neutron [7, 8] scattering have shown that even in the FM ground state, there are non-FM regions which are in a phase with SL order, but the identity of the phase has remained elusive. In order to fully understand CMR, it is important to know what this SL is, especially in comparison to the CO/OO/AF that occurs in the absence of FM.

Resonant elastic soft x-ray scattering (RSXS), which directly probes charge, orbital, and antiferromagnetic order, is an ideal tool for measuring SL order. Unlike other methods of measuring SL reflections, RSXS is resonant, so it can provide the energy dependence of a SL reflection intensity, which is a fingerprint for the ordered state that gives rise to the SL reflection [9–12]. Previous RSXS studies on $La_{1.5}Sr_{0.5}MnO_4$ [9], $Pr_{0.6}Ca_{0.4}MnO_3$ [10, 11], and $Pr_{0.7}Ca_{0.3}MnO_3$ [12] have shown that the ground state of these materials is CE type OO and AF, which is illustrated in the top half of Fig. 1. In these materials there is no metallic state to compete with the insulating OO/AF state.

We studied $La_{0.35}Pr_{0.275}Ca_{0.375}MnO_3$ (LPCMO), which undergoes a phase transition from a paramagnetic insulating (PI) state to a state with SL order at $T_{CO} \approx 210\,K$. LPCMO has a low-temperature ferromagnetic metallic (FM) ground state, with $T_C \approx 80\,K$ cooling and $120\,K$ warming [13]. It is the ideal material in which to compare the SL order that coexists with FM to that which exists independently, as the former is present below T_C, while the

latter exists above T_C. SL order in FM manganites has been linked to glassy polarons [14, 15], and we showed in Ref. [3] that the CO/OO/AF in LPCMO exhibits similar glassiness likely resulting from the same phenomenon, so our measurements below T_C are representative of all FM manganites. We chose the hole doping $x = 0.375$ because $La_{0.625}Ca_{0.375}MnO_3$ has the highest T_C in the $La_{1-x}Ca_xMnO_3$ series. In this letter, we use RSXS at the manganese $L_{2,3}$ edge to compare the SL order that is the dominant phase above T_C to that which coexists with FM below T_C in LPCMO.

A single crystal of LPCMO was grown by the floating zone method. We performed RSXS measurements at the at the Canadian Light Source (CLS), beamline ID10-2, using the REIXS endstation [16]. We measured at the manganese $L_{2,3}$ edge, using linear horizontal and vertical polarized light. The experimental geometry is shown in Fig. 2a. We performed our measurements at $160\,K$, which is above T_C, and at $50\,K$, which is below T_C. We chose these temperatures because there are no traces of FM at the former and the sample is entirely magnetized (except of course for the regions of SL order) at the latter [3].

In LPCMO, we focused on the $\left(0\,\frac{1}{2}\,0\right)$ and $\left(\frac{1}{2}\,0\,0\right)$ SL Bragg peaks. Figure 1 shows CE type CO/OO/AF, which is present in many manganites, and the SL peaks that it generates. The $\left(\frac{1}{2}\,0\,0\right)$ peak arises from AF, while OO generates the $\left(0\,\frac{1}{2}\,0\right)$ peak. Due to twinning in the sample, the $\left(0\,\frac{1}{2}\,0\right)$ and $\left(\frac{1}{2}\,0\,0\right)$ peaks are accessible from the same experimental geometry, and they are slightly offset in reciprocal space due to the difference in lattice constants. This offset is not large enough to resolve the two peaks separately, but we can take advantage of the resonant aspect of RSXS to investigate the contributions of different types of order to the SL peak.

To compare the ordered states that generate the two overlapping SL reflections, we measured the energy dependence at three values of q around the peaks: on the peak (q_0), at a lower q ($q_<$), and at a higher q ($q_>$). These results are plotted in Fig. 2. Figures 2c and 2d show the q and resonance profiles, respectively, of the $\left(0\,\frac{1}{2}\,0\right)$, $\left(\frac{1}{2}\,0\,0\right)$ SL peaks as measured above T_C. It is evident that the energy dependence of the diffracted intensity varies drastically with q, indicating the presence of multiple types of SL order. We will discuss the nature of this SL order in depth below.

Below T_C, the vast majority of the sample is in the FM state [3, 13], and the scattering tells a completely different story. The data are plotted in Figure 2e–f. The resonance profiles taken at $q_<$ and $q_>$ are practically identical, and the only difference between them and the
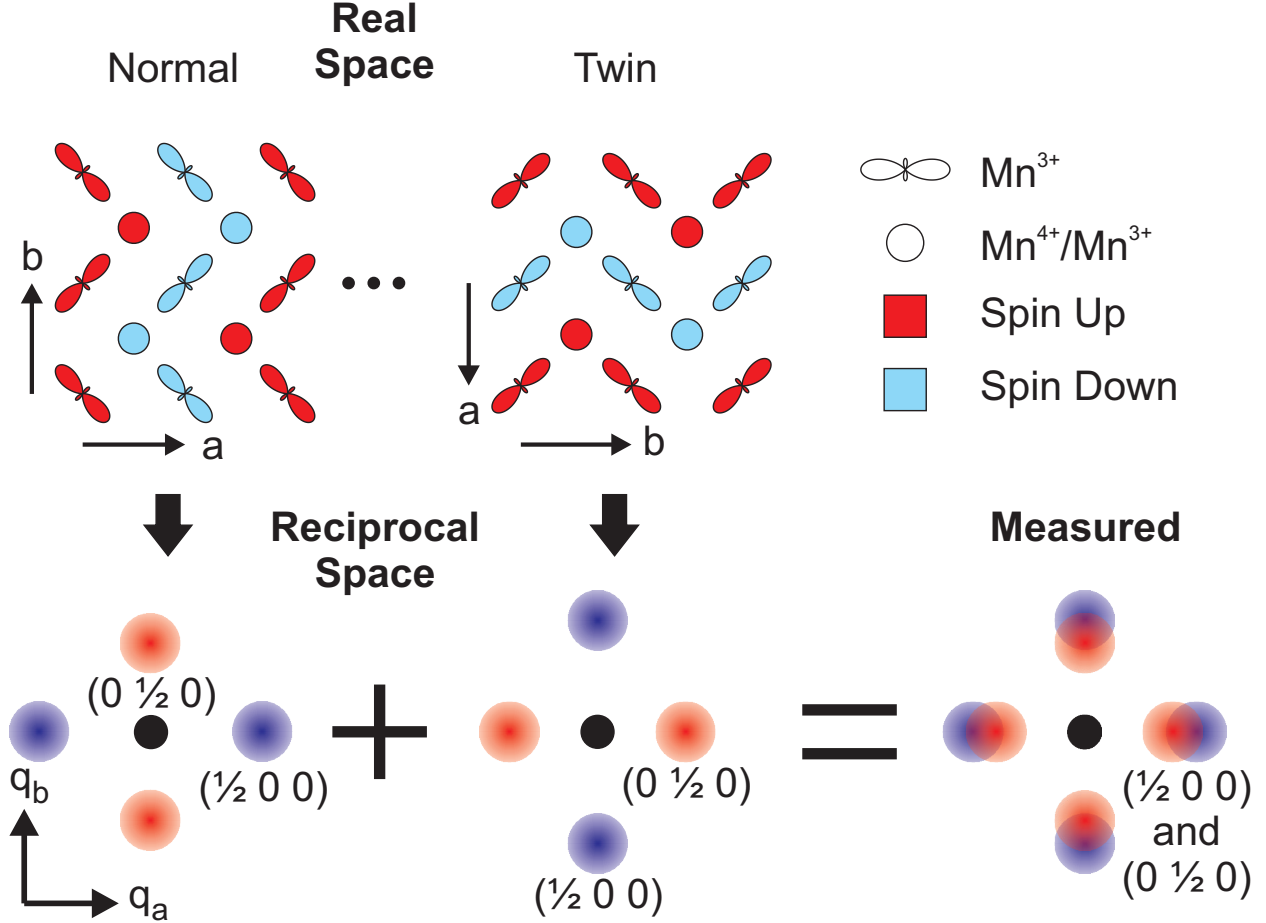
FIG. 1. (color online) Top left: the idealized picture of CE type orbital and magnetic order present in many manganites, including LPCMO. Note that OO and AF show up at different values of $\mathbf{q}$: OO modulates along the b axis and thus shows up at $q = \left(0\,\frac{1}{2}\,0\right)$, while AF modulates along the a axis and shows up at $q = \left(\frac{1}{2}\,0\,0\right)$. Top center: the twinned orientation. Our sample is crystallographically twinned, so both orientations shown are present. Bottom left and center: the relevant superlattice diffraction peaks in reciprocal space. $a < b$, so the magnitudes of q are different for the two peaks. Bottom right: the measured signal is a superposition of the normal and twin regions.

resonance profile measured at q_0 is the overall intensity. This is a clear indication that there is only one type of SL order at $q = \left(0\,\frac{1}{2}\,0\right), \left(\frac{1}{2}\,0\,0\right)$, and therefore the SL order that coexists with the FM state is not a combination of CO/OO/AF. Instead, the energies of the peaks are consistent with AF [11], but further measurements were required to confirm that we are not looking at an exotic form of CO or OO.
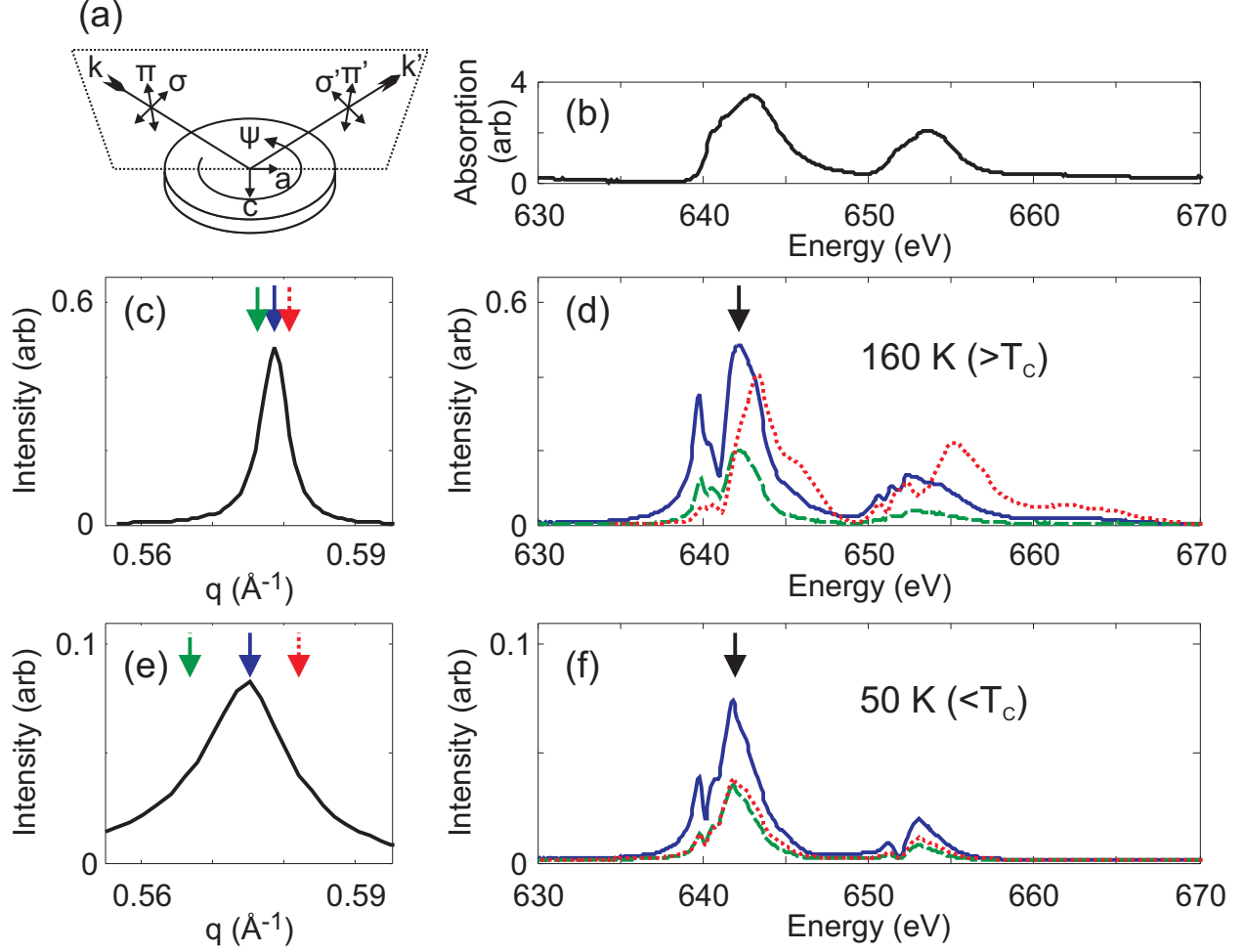
FIG. 2. (color online) (a) The experimental geometry. (b) An x-ray absorption spectrum taken at 160 K. (c) q and (d) energy dependence of the $\left(0\frac{1}{2}0\right)/\left(\frac{1}{2}00\right)$ peak intensity at 160 K on warming, which is above the T_C. The data were taken at $E = 642.2\,\text{eV}$ and $q_0 = 0.5788\,\text{Å}^{-1}$, respectively. The arrows in (c) indicate the values of $q_<$, q_0, and $q_>$, where we measured the energy dependence, and the arrow in (d) indicates the energy at which we measured the q dependence. (e), (f) the same as (c), (d), but at 50 K on cooling, just below T_C. The data were taken at $E = 642\,\text{eV}$ and $q_0 = 0.5752\,\text{Å}^{-1}$, respectively. All data in this figure were taken with π polarized incoming light.

To more thoroughly investigate the SL order present below T_C, we measured the azimuth (ψ) dependence of the scattered intensity. The results are plotted in Fig. 3. We defined the azimuth such that when $\psi = 0$, the c axis is perpendicular to the scattering plane, as illustrated in Fig. 2a. Following Ref. [17], we calculated that scattering due only to AF modulation of the magnetic moment along the c axis would have intensity proportional to
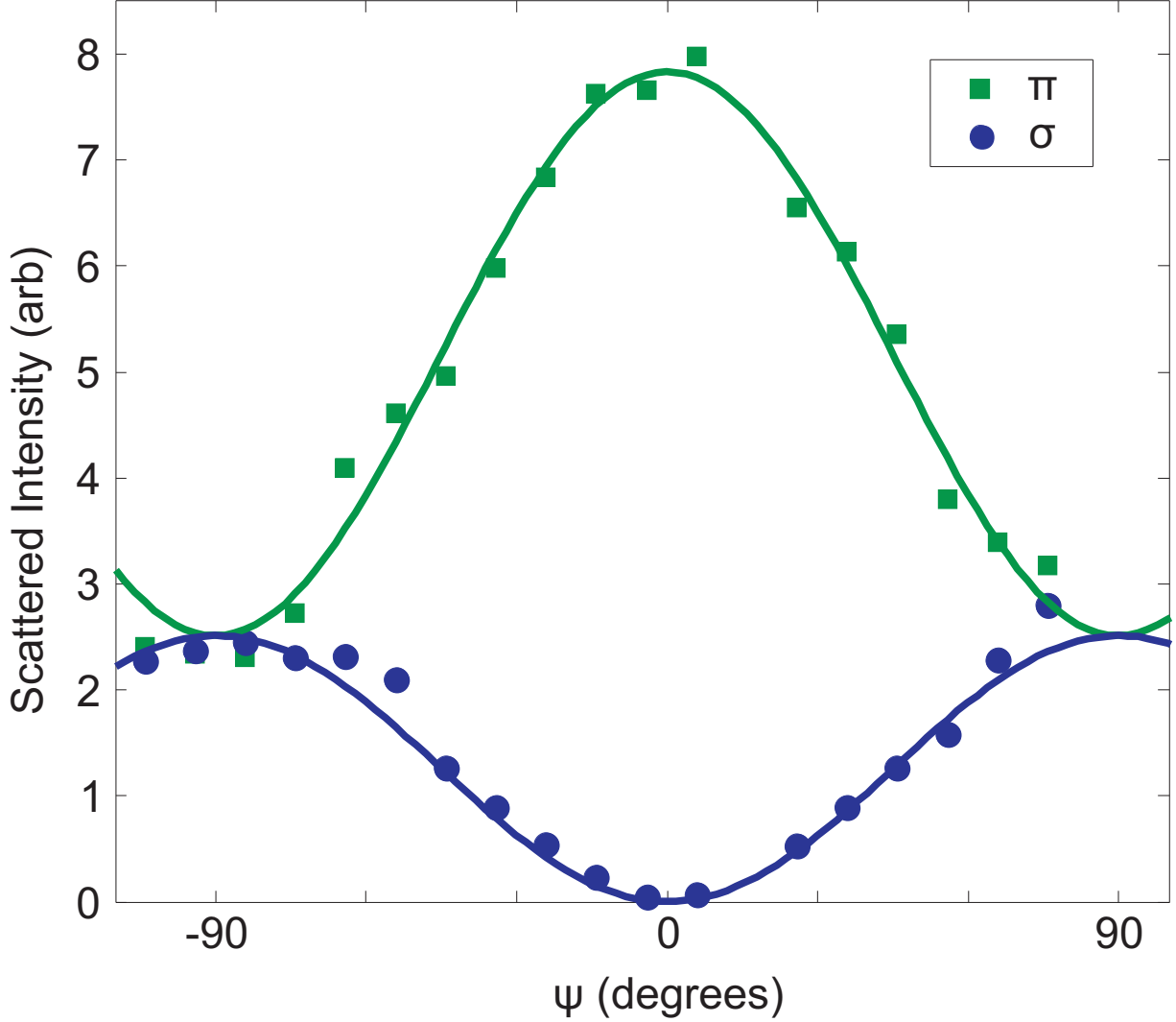
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FIG. 3. (color online) Azimuthal dependence of the scattered intensity, measured at 50 K with π and σ polarized light. $\psi = 0$ corresponds to the c axis being perpendicular to the scattering plane. Lines are the calculated intensity for a superlattice peak resulting solely from antiferromagnetism with the moment pointing along the c axis.

$\sin^2(\psi)\cos^2(\theta)$ for σ-polarized incoming light and to $\sin^2(\psi)\cos^2(\theta) + \cos^2(\psi)\sin^2(2\theta)$ for π-polarized incoming light. The lines in Fig. 3 are these functions, with the scattering angle $\theta = 67°$, corresponding to our experimental geometry. It is clear that the data agree with the calculation.

Now that we have determined that the resonance profile observed below T_C corresponds to AF, we can discuss the data taken above T_C more thoroughly. In particular, we note that the resonance profile taken at $q_<$ above T_C looks similar to those taken below T_C, as the peaks

in all of these measurements occur at similar energies and have similar relative intensities. On the other hand, the resonance profile taken at $q_>$ above T_C is very different from those taken below T_C, most noticeably at the high-energy end of the L_3 edge (643–648 eV) and of the L_2 edge (> 655 eV). We can thus assign the resonance profile at $q_<$ to AF and that at $q_>$ to OO. Comparison with the positions of peaks in resonance profiles measured on $Pr_{1-x}Ca_xMnO_3$ confirm the assignment [10–12]. If we were observing pure CE type order, we would expect the opposite: AF should show up at a higher q than OO does. This does not mean that CE type order is not present, but rather that the SL order is not completely spatially uniform. Above T_C, LPCMO contains regions of SL order and of the PI phase [13]. Since the SL order induces lattice distortions, there are regions of accommodation strain buffering the SL order and the PI regions [3, 18]. If the accommodation strain were more hospitable to AF than OO, it could produce an AF-only signal at a lower q than that of the main peak. Our inability to resolve multiple SL peaks is thus a result of the continuous variation of the lattice constant from the strained regions with CE type CO/OO/AF to the unstrained PI regions, and thus this scenario is consistent with a single SL peak.

One remaining question is whether another type of SL order coexists with the AF order below T_C. AF existing on its own would be mostly the result of the Goodenough-Kanamori rule, which governs nearest-neighbor AF coupling. Any AF that produces SL reflections at the q where we see them must have both ferromagnetic and antiferromagnetic nearest-neighbor couplings within the ab plane. For example, in the CE type order illustrated in Fig. 1, the periodic OO and lattice distortions determine the nature of the nearest-neighbor magnetic interactions, resulting in AF at $\left(\frac{1}{2}\,0\,0\right)$. Below T_C, we have shown that there is no OO at $\left(0\,\frac{1}{2}\,0\right)$, so there must be a different periodic mechanism that dictates the nearest-neighbor magnetic interactions. This has not been investigated in LPCMO, but there have been a few electron [5] and neutron [7, 8] diffraction studies on $La_{1-x}Ca_xMnO_3$ (LCMO), which like LPCMO has a FM ground state. In all of the studies, the experimenters found SL reflections at half-integer values of q. The experimenters could not determine the exact origins of these SL reflections, although in Refs. [5, 8] the authors suggest atomic displacements as a possible mechanism, and in Ref. [5] the authors propose a model of periodic atomic displacement waves. This model provides a mechanism to stabilize AF at the $q = \left(0\,\frac{1}{2}\,0\right), \left(\frac{1}{2}\,0\,0\right)$ below T_C and in the accommodation strain above T_C. While the atomic displacement does cause SL reflections at half-integer values of q, it does not do so

at the values of q that are accessible at energies around the Mn L_3 edge, so we could not measure it directly.

To summarize, we have observed that the superlattice order that coexists with the dominant ferromagnetic metallic state in LPCMO is substantially different from the CE type superlattice order that exists in LPCMO above T_C and in other manganites where no ferromagnetic state is present. Below T_C, the only superlattice order present at $q = \left(0\,\frac{1}{2}\,0\right), \left(\frac{1}{2}\,0\,0\right)$ is antiferromagnetic. This geometry of antiferromagnetism is not inherently stable, and we propose that the atomic displacement waves discussed in Ref. [5] are responsible for stabilizing the antiferromagnetism. Computational studies of manganites have shown that antiferromagnetism coexists with the ferromagnetic state [19, 20], but they have not produced an antiferromagnetic state that is consistent with our measurements. The coexisting phase is a critical component of CMR, and understanding its nature is a critical step towards to a complete theory of CMR and phase separation.

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