Universal features of charge and spin order in a half-doped layered perovskite.

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We have investigated the peculiar structure of charge and spin ordering in the half-doped layered perovskite oxide La1.5Sr0.5CoO4 by elastic neutron scattering. Two samples with different preparation histories were studied. We find that the generic features of the ordered states, such as their short-range, glassy nature and the spin incommensurability, are sample-independent. At the same time, some subtle features of the ordered phases, such as the correlation lengths, differ.

Recently much attention has been paid to exploring the charge/orbital- and spin-ordered phases in the charge-doped strongly-correlated transition-metal oxides, such as the superconducting cuprates and the magnetoresistive manganites (see Refs. 1, 2 for a review). Competition of the spin, orbital and/or the charge/valence degrees of freedom results in non-trivial ground states, such as a magnetic-field-driven metal-insulator transition, etc. At small doping, the charges often separate into lines, forming a stripe-like superstructure 3, which may be important for the high-temperature superconductivity in cuprates. At half-doping, x = 0.5, there is a natural opportunity for a robust valence-ordered state with the checkerboard filling of the two-dimensional (2D) square MO2 lattice (M = Cu, Mn, Ni, Co, ... is a 3d metal) by M2+/M3+ or M4+/M5+ ions. At high doping, close to x = 0.5, such a phase with the checkerboard charge order (CO) is often stabilized by the Jahn-Teller distortion, and is in competition with the metallic state where the charges are delocalized. Such a competition is at the heart of the strong response (CMR) of the doped pseudocubic manganites to a magnetic field, which favors the metallic phase by inducing ferromagnetism.

The CO and the spin-ordered (SO) phases were recently characterized in a number of the half-doped materials, in particular, in the layered perovskites La0.5Sr1.5MnO4 4, La1.5Sr0.5CoO4 4, 5, and La1.5Sr0.5NiO4 5. All three materials have the tetragonal crystal structure of the “HTT” phase (space group I4/mmm, see Fig. 1(a) in Ref. 5), and with lattice spacings that only differ by less than 1%. Although an “orthorhombic” indexing based on the space group F4/mmm, with a twice larger unit cell, \(2a \times 2a \times c\), is often employed to account for breaking of the translational symmetry in the a - b plane by the checkerboard CO superstructure, here we use the I4/mmm notation corresponding to the true crystal lattice.

With decreasing temperature, all three compounds first undergo a transition to the checkerboard charge-ordered state. It is accompanied by a dramatic increase of the activation energy in the T-dependence of the electrical conductivity, which is a clear evidence of the charge localization. An important generic feature of the CO in the layered materials at half-doping is its finite correlation range. It results from the combination of the random electrostatic potential introduced by the quenched disorder of the dopant ions, and the quasi-two-dimensional nature of the elastic couplings between the distortions in different layers. 6. If the coupling between the distortions is isotropic, as it is in the pseudo-cubic manganites, the CO may become a truly long-range superstructure.

In all three materials the spin ordering (SO) follows the charge order, but at a significantly lower temperature. In the manganite, La0.5Sr1.5MnO4, the SO is commensurate, with the propagation vector \(Q = (1/4, 1/4, 1)\) 6, as for the simple two-sublattice antiferromagnetism on each of the two fields of the CO checkerboard. In La1.5Sr0.5CoO4, which is the subject of this study, the SO was found to be incommensurate, with the propagation vector \(Q = (\zeta, \zeta, 1)\) with \(\zeta \approx 0.258\) 7. The situation is even more complex and intriguing in the nickelate. There the SO is also incommensurate, but with \(\zeta \approx 0.22\), smaller than 1/4, and is preceded by the transformation of the CO from a checkerboard to a stripe-like phase with the propagation vector \(Q = (2\zeta, 2\zeta, 0)\) 8.

The correlation lengths of spin and charge order measured in the above materials are summarized in Table 1. Both SO and CO are much better correlated in the manganite, where the SO is commensurate. Although a recent X-ray study 10 determined that \(\xi_{ab}^{(CO)} = 200(30)\) Å and \(\xi_{c}^{(CO)} = 30(2)\) Å in La0.5Sr1.5MnO4, these values are still about an order of magnitude larger than the CO correlation lengths for the other two compounds in Table 1. The situation with the SO correlation lengths is similar. Whether the spin incommensurability is in some way related with this difference in the correlation lengths, though, is not really clear. Furthermore, a question arises: is there any connection at all between the CO and SO correlation ranges for a given material?

The difference in the CO correlation lengths measured in different materials can readily be understood from the generic cross-over phase diagram based on the random field Ising model (RFIM). 3. It simply indicates that the effective random field and/or the inter-plane coupling in the quasi-2D anisotropic RFIM, which is the effective
TABLE I: Correlation lengths (in Å) of charge and spin order in three half-doped isostructural layered perovskite oxides.

| Material          | \(\xi_{ab}^{(CO)}\) | \(\xi_{c}^{(CO)}\) | \(\xi_{ab}^{(SO)}\) | \(\xi_{c}^{(SO)}\) | Ref. |
|-------------------|----------------------|----------------------|----------------------|----------------------|------|
| \(La_{0.5}Sr_{1.5}MnO_4\) | \(\gtrsim 300\) & \(\approx 50\) & \(\gtrsim 300\) & \(\approx 33\) & [5] |
| \(La_{1.5}Sr_{0.5}NiO_4\) | 30(10) & 2(1) & 120 & 13 & [8] |
| \(La_{1.5}Sr_{0.5}CoO_4\) | 23(3) & 8.3(6) & 79(3) & 10.7(3) & [6, 7] |

low-energy theory describing the CO transition, differ. However, because the source of the random field is the crystallographic disorder, it may also vary from one sample to another of the same material, with the same nominal stoichiometry. How strong is this effect, and how does it compare to the variation of \(\xi^{(CO)}, \xi^{(SO)}\) between the different materials?

To address these questions, we have studied two samples of the half-doped cobaltate, \(La_{1.5}Sr_{0.5}CoO_4\), of different size and with different preparation histories, using elastic neutron scattering. Sample #1 is a cylinder of \(m_1 \approx 0.5\) g and \(\approx 5\) mm long, prepared at Nagoya University as described in Ref. [11] and was previously studied in Refs. [2, 3]. A larger sample #2 is \(\approx 45\) mm long, \(m_2 \approx 11\) g cylinder, and was grown in air atmosphere in the floating zone furnace at Brookhaven National Laboratory. Both samples were a high quality single crystals with mosaic spread of less than 0.25°. Within the accuracy of our measurement they both have the same low \(T\) lattice constants, \(a = 3.830(3)\) Å and \(c = 12.51(2)\) Å.

Measurements of the wave-vector dependence of the elastic scattering associated with charge and spin ordering were performed on the BT2 spectrometer at NIST Center for Neutron Research. The incident and the scattered neutron energy, \(E_i = E_f = 14.7\) meV, was defined by PG(002) reflections, with two PG filters suppressing the higher-order contamination. Beam collimations were \(\approx 60'\) and \(\approx 100'\) before the monochromator and after the analyzer, respectively, and \(20' - 20'\) around the sample. The sample was mounted in a dispplex refrigerator with its horizontal scattering plane, and kept at \(T = 10(2)\) K. To establish the similarity of the temperature dependence of the SO scattering in the two samples, some additional measurements were performed using the SPINS cold-neutron spectrometer.

The dependence of the CO scattering on the wave vector transfer along the \(c\)-axis for the two samples is shown in Fig. 1 (left panel, sample #1; right panel, #2). The scans through the CO peaks at \(Q = (h + 0.5, h + 0.5, l)\) in the \(ab\)-plane, differ essentially only in their intensity, and are not shown. The CO diffuse scattering was analyzed following the procedure described in the Ref. [2]. The solid curves in Figure 1 show the corresponding resolution-corrected fits to the “lattice Lorentzian” scattering function which describes the diffuse scattering by a short-range superstructure (shaded areas show the calculated intensity in the absence of the background).

It is clear from Figure 1 that the long-period \(l\)-dependence of the diffuse intensity is similar in both samples. This indicates that in both cases it results from the same kind of local distortion of the CoO\(_6\) octahedra. In fact, the fit shows that the corresponding displacements of the oxygen and Sr/La ions are, within its accuracy, the same in both samples, \(\epsilon_{O(1)} = 0.044(4)\) Å, \(\epsilon_{O(2)} = 0.080(8)\) Å, and \(\epsilon_{Sr/La} = 0.010(2)\) Å (cf. Refs. [4, 11]). Here we have allowed for a small modulation of the La/Sr position which slightly improves the fit). What makes the scattering patterns from the two samples look quite distinct, is the difference in the CO correlation

![FIG. 1: Dependence of the structural elastic diffuse scattering accompanying the charge order on the wavevector transfer along the c-axis in two samples. Al(111), Al(200) and Al(220) mark the corresponding peaks arising from the “parasitic” scattering by the aluminium in the sample environment.](image)

![FIG. 2: Incommensurate magnetic peaks arising from the short-range spin order in two samples. (a) #1, and (b) #2. Temperature dependence of the magnetic intensity is essentially identical in both cases, with an onset at \(T_s \approx 30\) K.](image)
range between the \(ab\) planes, \(\xi_{c}^{(CO)}\).

The correlation lengths for the charge \(\left[\xi_{ab}^{(CO)}, \xi_{c}^{(CO)}\right]\) and the spin order \(\left[\xi_{ab}^{(SO)}, \xi_{c}^{(SO)}\right]\) refined from our measurements are summarized in Table II. The inter-plane CO correlation length in the sample \#1 is somewhat larger than the distance between the neighboring \(ab\) planes, \(c/2\), and the CO peaks at integer \(l\) are well separated. On the other hand, in the case of sample \#2 there are no such well-defined peaks. This means that the inter-plane correlations are not developed at all, i.e. the correlation length is much smaller than the distance between the neighboring \(ab\) planes. In our refinement we fixed \(\xi_{c}^{(CO)} = 2.5\) Å. At the same time, the CO correlation range within the \(ab\) layers is essentially the same for both samples. This agrees with the expectation from the anisotropic RFIM \(\xi\). In the strongly anisotropic regime, \(\xi_{c}^{(CO)}/\xi_{ab}^{(CO)} \ll 1\), the in-plane correlation length, \(\xi_{ab}^{(CO)}\), is essentially determined by the 2D RFIM physics, and is not sensitive to the developing inter-plane correlations.

Typical scans characterizing the dependence of the magnetic scattering associated with the spin order on the wave-vector transfer in the \(ab\) plane are shown in the Figure 2. The solid lines are the appropriate resolution-corrected “lattice Lorentzian” fits, as in Ref. 8. The spin structure is described as a damped flat spiral polarized in the \(ab\) plane, with the propagation vector \(Q = (\zeta, \zeta, 1)\). The \(q\)-scans (not shown) have much broader peaks centered at odd \(l\) (the inter-plane SO correlation length, \(\xi_{c}^{(SO)}\), is also much shorter than that in the plane, \(\xi_{ab}^{(SO)}\)). They are also well described by the model.

Although the charge order is somewhat better correlated in sample \#1, the refinement shows that the spin order correlation lengths are appreciably, by more than a factor of 1.5, larger in sample \#2. This supports the conclusion that, although the CO correlation range in the \(ab\) plane is quite short, the resulting disorder is still far from the 2D percolation threshold for the spin system. Therefore, it is not the source of the SO finite correlation length which, most probably, originates from the frustrated spin interactions \(\xi\). This conclusion is further corroborated by the observation that the SO incommensurability \(\zeta\) appears smaller in the sample \#2, where the spin correlations are appreciably stronger (although the difference is small, it is well beyond the most conservative error bars which are shown in Table III).

To summarize, we find that the generic, qualitative features of the charge and spin ordering in the half-doped layered perovskite \(\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_{4}\), such as their short-range, glassy nature and the spin incommensurability are common for the two samples that we have studied. In fact, they are also shared by the other layered half-doped materials (Table I). However, we also find some appreciable differences between our two samples with different preparation histories. The most dramatic is the difference in the correlation lengths. While the in-plane CO correlations are essentially the same, the CO correlation between the layers is significantly weaker in the sample \# 2. This can be understood on the basis of the anisotropic RFIM \(\xi\) that describes the charge ordering in the half-doped materials. It implies that the weak residual inter-layer CO coupling is sensitive to the impurities and the imperfections in the crystal and is sample dependent.

For the spin order, the correlation lengths are as different between the two samples, as those between the sample \#1 and the nickelate, \(\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_{4}\). In fact, the correlation lengths of the checkerboard charge order and of the SO in the nickelate are essentially the same as in our sample \# 2 of \(\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_{4}\). The spin incommensurability, though, is completely different, and the charge-stripe phase is not present in either of the cobaltate samples. Finally, the smaller incommensurability \(\zeta\) in the sample \#2 with stronger spin correlations seems to indicate that these are related, and, perhaps, \(\zeta\) vanishes if the SO is truly long range. This may explain, why the spin structure is apparently commensurate in the manganite, \(\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_{4}\), where the SO correlation length is at least twice larger than in our sample \#2.

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### Table II: Charge and spin order correlation lengths (Å) and the spin incommensurability \(\zeta\) (lattice units) observed in two different \(\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_{4}\) single crystal samples.

| Sample       | \(\xi_{ab}^{(CO)}\) | \(\xi_{c}^{(CO)}\) | \(\xi_{ab}^{(SO)}\) | \(\xi_{c}^{(SO)}\) | \(\zeta\)  |
|--------------|----------------------|---------------------|---------------------|---------------------|---------|
| \# 1 (small) | 19(2)               | 8(1)                | 79(3)               | 9(1)                | 0.258(1) |
| \# 2 (large) | 18(1) \(\leq 2.5\) (fixed) | 125(6) \(16\) \(15.5\) | 0.255(1)           |                     |         |

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