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Spin and Charge Order in Single-Layered Provskite Cobaltates

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Recent neutron scattering studies on charge and spin ordering in $\mathrm{Pr}_{2-x}\mathrm{Ca}_x\mathrm{CoO}_4$ ($0.39 \leq x \leq 0.73$) and $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CoO}_4$ ($x = 0.61$) are reviewed. We found that the propagation vectors of the charge and spin order for both systems are (2δ,0,1) and (δ,0,1), respectively, in the orthorhombic notation with lattice constants $a = 5.392$ Å and $c = 12.196$ Å. δ is linearly proportional to $1-x$ for $x > 0.5$, $\delta = 1-x$, but it is 0.5 for $0.39 \leq x \leq 0.5$. This indicates that while the checkerboard charge ordered state previously observed in $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CoO}_4$($x = 0.5$) is also realized in $\mathrm{Pr}_{2-x}\mathrm{Ca}_x\mathrm{CoO}_4$ with $0.39 \leq x \leq 0.5$ and $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{CoO}_4$ ($x = 0.61$), the charge ordered state for $x > 0.5$ is different from the checkerboard order. Instead, our results suggest that for $x > 0.5$, a charge-density-wave-like modulation of Co^{2+} and Co^{3+} ions occurs in the Co-O plane and that ferromagnetic stripes formed at the Co^{2+} sites along the b-axis are antiferromagnetically arranged along the a-axis.

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I. INTRODUCTION

One of the most intriguing phenomena in physics is the anomalous metallic state, such as high-Tc superconductivity and colossal magnetoresistivity, that emerges when charge carriers are doped into a Mott insulator. A Mott insulator is a material that is insulating due to strong Coulomb repulsions between electrons, even though it has partially filled electronic bands and band theory would predict it to be metallic. Virtual charge fluctuations in a Mott insulator generate a super-exchange interaction between the spins of unpaired electrons of neighboring ions, which leads to long-range antiferromagnetic order in many materials. Doping (adding charge carriers to) a Mott insulator induces a phase transition to metallic phases whose properties cannot be explained in terms of conventional metal physics.

Since the discovery of charge and spin stripes in a cuprate, self-organization of the electrons in transition metal oxides and its relevance to high-Tc superconductivity have been among the central issues in condensed matter physics. Several types of electronic superstructures have been found in single-layerd perovskite cuprates [1, 2], isostructural nickelates [3–5], and even manganites [6], which poses a fundamental question whether the formation of electronic superstructures is essential in the physics of doped Mott insulators [6]. Theories suggest that the competition between the kinetic energy of the holes, the Coulomb interactions between the holes, and the magnetic interactions between spins leads to self-organized charge and spin inhomogeneities on a mesoscopic scale. Unfortunately, experimental evidence to date is limited only to aforementioned three examples of transition-metal oxides [7,8] and it is important to expand the scope of research over other unexplored transition-metal oxides in order to elucidate the generality and role of the self-organization of charge and spin degrees of freedom. Furthermore, the doped cuprates and nickelates studied so far are in the region of concentrations less than 0.5, at which the number of the excess charges is one half that of the transition-metal ions, thus, a checkboard ordering of spin and charge is expected. It is important to investigate how the mesoscopic self-organization behaves when the concentration becomes larger than 0.5.

We have studied the $\mathrm{K}_2\mathrm{NiF}_4$-type single-layered cobalt oxides, $\mathrm{R}_{2-x}\mathrm{A}_x\mathrm{CoO}_4$ (R = Rare earth and A = Alkali earth ion), with x around 0.5. The two-dimensional perovskite cobaltate, $\mathrm{R}_{2-x}\mathrm{A}_x\mathrm{CoO}_4$, is a charge-transfer-

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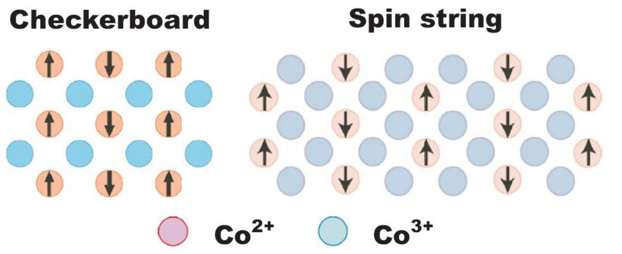

Fig. 1. Schematic models for the checkerboard-type spin-charge order (left) and the spin string order (right) in PCCO.

type insulator, in which doped holes can change the undoped Co^{2+} ($3d^7$: $t_{2g}^5 e_g^2$: S = 3/2) state to a Co^{3+} ($3d^6$) state. Due to the crystal splitting (Δ) between the doubly degenerate e_g and the triply degenerate t_{2g} levels, the Co^{3+} ($3d^6$) ion has, as its ground state, a t_{2g}^6 electronic configuration, and a nonmagnetic low spin (S = 0) state. When the temperature increases, the spin state can change to a magnetic state because the crystal field splitting (Δ) is relatively small, an order of 10-20 meV, thus, upon warming, the electrons can be excited to the e_g levels, which can make the Co^{3+} ion magnetic. Possible magnetic states are the intermediate spin state ($t_{2g}^5 e_g^1$; S = 1) and the high spin state ($t_{2g}^4 e_g^2$; S = 2), and it is still in controversy which state is lower in energy [9–13]. It is an interesting problem how the spin and charge pattern observed for the $x = 0.5$ sample of $La_{2-x}Sr_xCoO_4$ would be affected by the thermally excited spin state of Co^{3+} ions.

Resistivity measurements on LSCO with $0.0 \leq x \leq 1.5$ [14] suggested that in the insulating phase charge orders. Indeed, neutron scattering measurements on the insulating LSCO ($x = 0.5$) have found the checkerboard-type spin-charge order (CBO) shown in the left panel of Figure 1, which develops below 800 K [10,15]. The checkerboard spin-charge order (CBO) can be considered as the limit of the stripe charge order (STO) in which the spacing of the hole stripes is shortest. Since the stripe spacing is controled by the hole (or electron) concentration, for $x \neq 0.5$, the charge ordering pattern can be different from the checkerboard pattern.

In this paper, we report our results of neutron diffraction measurements performed on the two-dimensional cobaltates $Pr_{2-x}Ca_xCoO_4$ (PCCO) ($0.39 \leq x \leq 0.73$) and $La_{2-x}Sr_xCoO_4$ (LSCO) ($x = 0.61$) to study their charge and spin states as a function of the concentration of the charge carrier. Prior to the neutron diffraction measurements, we confirmed that the electronic transport property and the magnetic susceptibility of the PCCO system were essentially identical with the previously reported behaviors of LSCO. Our main results are the following: For $0.39 \leq x \leq 0.5$ where the hole concentration is less than, but close to, $x = 0.5$, the spin and charge order in the cobaltates is a checkerboard-type order shown in Figure 1(a). On the other hand, for $x > 0.5$ where the hole concentration is larger than half the number of Co sites, incommensurate (IC) peaks appear with two characteristic wave vectors, $(\delta, 0, 1)$ and $(2\delta, 0, 1)$, with $\delta = 1 - x$. From their Q-dependences, we identified the IC peaks with $(\delta, 0, 1)$ to be magnetic and those with $(2\delta, 0, 1)$ to be structural. This indicates that the charge and spins form stripes as shown in Figure 1(b). This stripe order is similar to those observed in the underdoped region of cuprates and nickelates. It is, however, noted that in the overdoped ($x > 0.5$) cobaltates, the magnetic Co^{2+} ions form domain boundaries that separate the nonmagnetic Co^{3+} ions.

II. EXPERIMENTAL DETAILS

Single crystals of PCCO ($0.39 \leq x \leq 0.73$) and LSCO ($x = 0.61$) were grown by using the floating zone method, and the absence of impurity phases was confirmed by powder X-ray diffraction measurments. The hole concentration was evaluated by using the inductively coupled plasma method to determine the actual chemical composition, and the uniformity of the samples was examined by using the scanning electron microscopy. The high-quality single-crystal samples were cut into a typical size of $\sim$6 mm$^{\phi}$ in diameter and $\sim$20 mm in length for neutron diffraction experiments, and the profiles of the fundamental nuclear Bragg reflections were examined to assure that the mosaics of all the sample crystals showed resolution-limited sharp peaks, indicating high-quality crystals. Characterization of the bulk properties was carried out by using resistivity and magnetic susceptibility measurements with a Quantum Design PPMS and a MPMS SQUID magnetometers, respectively. Elastic neutron scattering experiments were performed on the 4G and 5G 3-axis thermal neutron spectrometers at the Japan Research Reactor-3 (JRR-3) at the Japan Atomic Energy Agency (JAEA), Tokai, Japan, and the BT9 spectrometer at the NIST Center for Neutron Research in the National Institute of Standards and Technology. The incident neutron beam was fixed at $k_i \simeq 2.67$ Å. The crystals were mounted in the $(h0l)$ reciprocal lattice plane in the orthorhombic notation with the lattice constants $a = 5.392$ Å and $c = 12.196$ Å. To index the peaks due to the charge and spin in PCCO and LSCO, it is convenient to choose a unit cell that corresponds to the orthorhombic phase, and we adopt this notation throughout the paper. The cylindrical sample was mounted either in a closed-cycle He gas refrigerator ($T \geq 0.7$ K) or in a vacuum furnace ($T \leq 800$ K).

III. RESULTS AND DISCUSSION

Figure 2 shows some of our inelastic neutron scattering data obtained from single crystals of PCCO ($x = 0.46$ and 0.66). The PCCO ($x = 0.46$) sample exhibits magnetic superlattice peaks at $\boldsymbol{Q}_{\mathrm{m}} = \boldsymbol{G} \pm (\delta_{\mathrm{m}}(x), 0, l)$. Here,

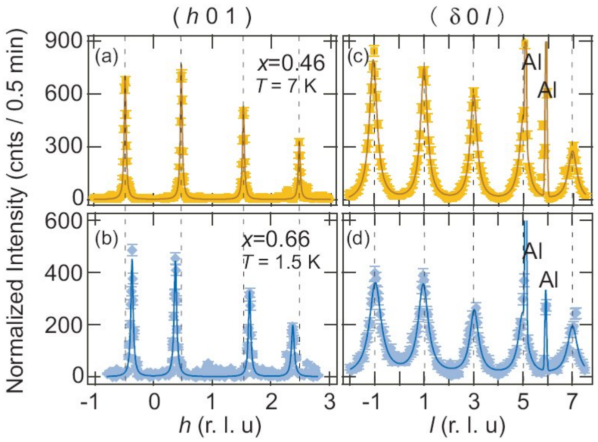

Fig. 2. Survey of the elastic magnetic scattering in the $(h0l)$ reciprocal plane. In-plane profiles (a,b) and inter-plane profiles (c,d) obtained from PCCO ($x = 0.46$ (yellow) and 0.66 (light blue)). The nonmagnetic background was measured at temperatures above the ordering temperatures and was subtracted.

$\boldsymbol{G}$ represents the fundamental nuclear reflections, and $\delta_{\rm m}(x)$ denotes an incommensurability of the in-plane spin order, which depends on x, while l denotes the commensurate odd integer positions. The incommensurability was $0.5 - \delta_{\rm m} = 0.026$ for $x = 0.46$ at 7 K and 0.14 for $x = 0.66$ at 1.7 K. Similar magnetic superlattice peaks were observed in all single crystals of PCCO for the concentrations that were studied ($0.5 < x \leq 0.73$).

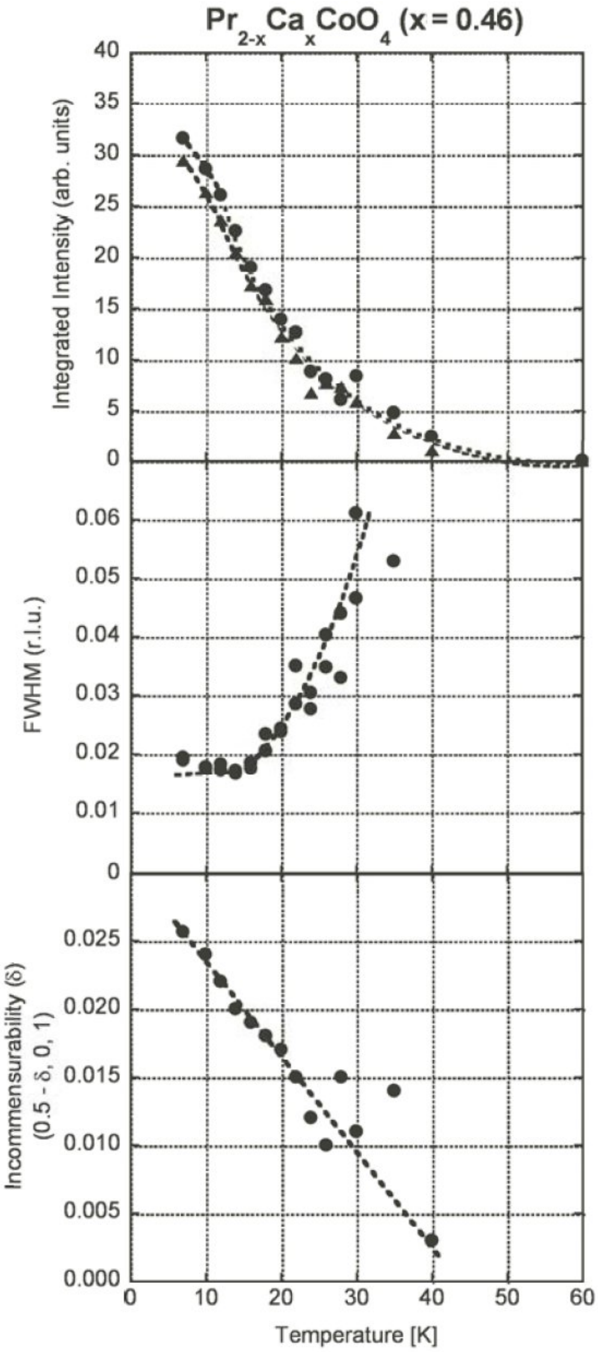

Fig. 3. Temperature dependence of (a) the integrated intensity observed at $Q = (\pm h,\ 0,\ 1)$, (b) the full width at half maximum, and (c) the incommensurability of the magnetic peaks observed from a single crystal of PCCO ($x = 0.46$).

Figure 3 summarizes the temperature dependences of the integrated intensity, the full width at the half maximum (FWHM), and the incommensurability of the magnetic peaks observed in PCCO ($x = 0.46$). As shown in Figure 3(a), magnetic ordering occurs around 40 K for $x = 0.46$. It is also noted that the incommensurability $\delta_{\rm m}(x)$ gradually changes from incommensurate at low temperatures to almost commensurate upon warming. δ close to 0.5 indicates that the spin and charge order is of the checkerboard type shown in Figure 1, which is essentially the same as the ordering pattern that observed in the LSCO ($x = 0.5$) sample. Also the checkboard-type ordering might be favored by the thermally excited magnetic states of Co^{3+} ions, which may explain the temperature dependence of δ. The FWHM plotted in Figure 3(b) was obtained by fitting the data to a Lorentzian without correction for the instrumental Q-resolution, which was about 0.018 r.l.u. As one can see in Figure 3(b), the FWHM decreases with decreasing temperature and becomes resolution-limited at low temperatures, indicating that the checkerboard order in the *ab*-plane gradually changes from short-ranged to long-ranged upon cooling. On the other hand, along the *c*-axis, the peaks are broad (see Figures 2(c) and (d)). This indicates that the correlations are short-ranged out of the *ab*-plane. A similar behavior of the checkerboard order has been previously observed in LSCO ($x = 0.5$) [15]. The interplane correlation lengths of the spin order can be estimated by using $\xi = 2/FWHM$; $\xi_c \simeq 7$ Å for PCCO ($x = 0.46$). This is slightly shorter than the $\xi_c \simeq 10.7$ Å obtained for LSCO ($x = 0.5$) [15]. This very short interplane correlation length for both systems indicates the two-dimensionality of the magnetic interactions.

The PCCO ($x = 0.66$) sample, on the other hand, exhibits magnetic peaks that are distinctly away from the commensurate positions, as can be seen in Figure 2(b). The position of the incommensurate magnetic peak $\boldsymbol{Q}_{\mathrm{m}}$ shifts systematically from $\delta_{\mathrm{m}}(x) \sim 0.44$ for $x = 0.56$ to $\delta_{\mathrm{m}}(x) \sim 0.36$ for $x = 0.66$ as x increases. We have also performed similar scans in the $(h, 0, l)$ reciprocal plane with larger Q and found superlattice peaks associated with charge order. The additional peaks were observed at $\boldsymbol{Q}_{\mathrm{c}} = \boldsymbol{G} \pm (2\delta_{\mathrm{c}}(x), 0, l')$, whose position also changed systematically with x. The charge peaks were very weak and diffusive and could only be observed at large Q. Unlike the magnetic peaks $\boldsymbol{Q}_{\mathrm{m}}$ that exhibit a weak temperature dependence, the charge order peaks with $\boldsymbol{Q}_{\mathrm{c}}$ show no detectable temperature dependence below 300 K.

IV. CONCLUSIONS

In conclusion, we have explored charge and spin ordering patterns in PCCO and LSCO as a function of the hole concentration and have demonstrated the existence of the checkerboard-type spin-charge order for $0.39 \leq x \leq 0.5$ in PCCO. The ordering pattern changed to the spin string-like order for $x > 0.5$, as shown in the right panel of Figure 1. The observed spin string-like order consists of one-dimensional ferromagnetic spin alignment on the Co^{2+} ion sites whose texture is formed by the charge ordering at temperatures higher by an order of magnitude than the charge ordering temperatures observed in nickelates and cuprates.

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