Magnetic impurity effect on charge and magnetic order in doped La$_{1.5}$Ca$_{0.5}$CoO$_4$

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Abstract. Neutron scattering experiments were performed on single crystals of magnetic impurity doped cobalt oxides La$_{1.5}$Ca$_{0.5}$CoO$_4$ to characterize the charge and spin orders. We newly found contrasting impurity effects. Two types of magnetic peaks are observed at $q=(0.5,0,L)$ with $L$=half-integer and integer in La$_{1.5}$Ca$_{0.5}$CoO$_4$, while magnetic peak at $L$=half-integer (integer) was only observed in Mn (Fe)-substituted sample. Although Mn and Fe impurities degrade charge and magnetic order, Cr impurity stabilizes the ordering at $x=0.5$. Based on the crystal structural analysis of Cr doped sample, we found that the excess oxygen and change of octahedron around Co$^{3+}$ were realized in Cr doped sample.

1. Introduction

Layered transition metal oxides have attracted much attention due to their wide variety of magnetic, electrical and structural properties. In some of the doped transition metal compounds, there is a real space ordering due to the charge carriers in a certain carrier concentration, resulting in an orbital ordering (OO) and sometimes a charge ordering (CO). In a neutron scattering study, Zaliznyak et al. investigated a checkerboard charge order of Co$^{2+}$/Co$^{3+}$ and Co$^{2+}$ magnetic order in the half-doped cobaltate La$_{1.5}$Sr$_0.5$CoO$_4$ [1]. From the analysis of the magnetic and charge order scattering, they concluded a checkerboard arrangement of Co$^{2+}$ and non-magnetic Co$^{3+}$ ions in the CoO$_2$ plane. However, Y. Moritomo et al. reported the drastic change of effective moment $\mu_{\text{eff}}$ in La$_{2-x}$Sr$_x$CoO$_4$($0.4<$x$<1.0$), suggesting a spin-state transition of Co$^{3+}$ ions from the high-spin to intermediate spin state [2]. Thus, spin state of Co$^{3+}$ is still controversial.

Recently, Fujita et al. found that Fe substitution significantly enhanced the charge and spin density wave in La$_{2-x}$Sr$_x$CuO$_4$(x=1/8) [3]. This result indicates that dynamical charge stripes can be stabilized into static ones. Although spin state of Co$^{3+}$ ions was determined as low-spin state by previous neutron scattering measurements, we considered that Co$^{3+}$ ions were not non-magnetic but paramagnetic state because of magnetic susceptibility measurements. Based on this report, we expected that paramagnetic Co$^{3+}$ spin can be stabilized by tiny magnetic impurities. In this paper, we report the magnetic impurity effect of spin and charge ordering in La$_{1.5}$Ca$_{0.5}$CoO$_4$.

2. Experimental procedure

Polycrystalline samples were prepared by solid-state reaction. First, stoichiometric mixture of La$_2$O$_3$, CaCO$_3$, CoO, Cr$_2$O$_3$, Mn$_2$O$_4$ and Fe$_2$O$_3$ powders were ground and calcined at 1200°C for 24h in N$_2$.
atmosphere. After repeating this grinding and sintering process two times, the powder sample was pressed into rod with a size of 8mmφ×100mm and sintered at 1200°C for 24h. Single crystals of nominal composition of \( \text{La}_{1.5}\text{Ca}_{0.5}\text{Co}_{0.97}\text{M}_{0.03}\text{O}_4 \) \((M = \text{Cr}, \text{Mn}, \text{Fe})\) were grown by floating zone method at feeding speed of 3mm/h in air. The ceramic compounds were confirmed to be a single phase using x-ray powder diffraction. The cylindrical crystals studied here for neutron scattering were about 6mm in diameter and 25mm in length. The crystal has a checkerboard charge order on \( \text{Co}^{2+}/\text{Co}^{3+} \). In this paper we use a unit cell with dimensions \( a_{\text{co}} \times a_{\text{co}} \times c \) (e.g. \( a_{\text{co}} \sim 5.436\text{Å}, c \sim 12.373\text{Å} \) for Cr doped sample).

Neutron scattering experiments were carried out on triple-axis spectrometer AKANE and powder diffractometer HERMES in Japan Atomic Energy Agency, Tokai. A combination of Ge(3,1,1) monochromator and PG(0,0,2) analyzer was employed for AKANE and no filters were attached owing to forbidden Ge (6,2,2) reflection. The incident energy of AKANE was fixed to be \( E_i = 19.4\text{meV} \), typical with a sequence of collimations of guide(20')-open-S-60'-blank(180'). The sample was mounted in a \(^4\text{He}-\text{cycle–type refrigerator, allowing wave vector transfer in the (H, 0, L) scattering plane. The wavelength of the neutron beam of HERMES was} 1.8484\text{Å}, \text{monochromatized by Ge(331). The fine powder samples were sealed in a vanadium cylinder (Φ10mm) with helium gas, and mounted on the cold head of a \(^4\text{He}-\text{cycle–type refrigerator.}}\)

### 3. Result and Discussion

Figure 1 shows \((h, 0, 1)\) scans in nominal composition of \( \text{La}_{1.5}\text{Ca}_{0.5}\text{Co}_{0.97}\text{M}_{0.03}\text{O}_4 \) \((M = \text{Cr}, \text{Fe}, \text{Mn})\). Peaks due to checkerboard charge order of \( \text{Co}^{2+}/\text{Co}^{3+} \) were observed in all samples. Indeed this order persists up to room temperature (not shown). The normalized intensity of the Charge ordered peak was much stronger in Cr doped sample, however clear enhancements were not detected in the case of Fe and Mn doping. This result suggests that Cr doping effectively stabilized the checkerboard charge order. Figure 2 shows Magnetic scattering at \((0.5, 0, L)\) in (a) pristine \( \text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4 \) [4] and (b) Cr (c) Fe (d) Mn doped \( \text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4 \). In pristine sample, two types of magnetic peaks are observed at \( q = (0.5, 0, L) \) with \( L \) = half-integer and integer in \( \text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4 \). On the other hand, magnetic impurity doping process drastically changes the magnetic diffraction pattern. The magnetic peaks with \( L \) = half-integer appear in Cr and Mn doping, whereas it switched to the reflection with \( L \) = integer in Fe doping. In order to determine correlation length of in plane and out of plane, the profiles of the charge order peaks are fitted to a Lorentzian form. We summarize the Neel order temperature and the correlation length of spin and charge ordering in table I. Although Mn and Fe impurities degrade charge and magnetic order, Cr impurity stabilizes the ordering at \( x = 0.5 \). For example, correlation lengths of charge and magnetic order along c-axis of Cr doped system \( (\xi_{\text{mag}} = 139(7)\text{Å}, \xi_{\text{co}} = 129(5)\text{Å}) \) are much larger than those of LCCO system \( (\xi_{\text{mag}} = 22(1)\text{Å}, \xi_{\text{co}} = 59(2)\text{Å}) \). This result suggests that that \( \text{Co}^{3+} \) site is selectively replaced by \( \text{Cr}^{3+} \).

| \( T_x (\text{K}) \) | \( L = \text{half-integer} \) | \( L = \text{integer} \) |
|-----------------|-----------------|-----------------|
| \( \xi_{\text{mag}}(\text{Å}) \) | \( \xi_{\text{co}}(\text{Å}) \) | \( \xi_{\text{mag}}(\text{Å}) \) | \( \xi_{\text{co}}(\text{Å}) \) |
| LCCO | 52 | 115(12) | 59(2) | 192(4) | 22(1) | 98(2) | 22(1) |
| Cr doping | 52 | 124(10) | 129(5) | 219(6) | 139(7) | 56(2) | 8(1) |
| Fe doping | 45 | 76(4) | 19(1) | 86(2) | 35(2) |
| Mn doping | 50 | 74(4) | 24(1) | 86(2) | 35(2) |

**Fig.1** Checkerboard charge order peak in impurity doped \( \text{La}_{1.5}\text{Ca}_{0.5}\text{Co}_{0.97}\text{M}_{0.03}\text{O}_4 \) with \( M = \text{Cr}, \text{Fe} \) and Mn (nominal composition).
To understand this mechanism from a view of crystal structure, we carried out neutron powder diffraction measurements on Cr doped sample. The diffraction data was analyzed by using the Rietveld analysis program RIETAN2000 [5]. The crystal structure parameters of Cr doped sample are listed in Table II. The diffraction pattern of Cr doped sample indicates an orthorhombic structure with the space group \(A2mm\) at 10K. It should be noticed that excess oxygen is incorporated at an interstitial site between LaO layers. By Cr doping, \(c\)-axis changes from 12.313(6)Å to 12.373(6)Å. This result supports the incorporation of oxygen into interstitial site. The \(c\)-axis of Mn and Fe doping sample that is determined by triple-axis spectrometer is 12.366 Å and 12.336 Å, respectively. The enhancement of \(c\)-axis can be explained by incorporation of excess oxygen. From above result, excess oxygen is an important factor to understand the drastic change of magnetic structure. As shown in Table II, two Co sites are separated to two independent sites and are arranging a checkerboard charge ordering pattern. The average Co(1)-O bond length of in-plane and out of plane are 1.91(2)Å and 2.035(6)Å, respectively. On the other hand, those of Co(2)-O bond length are 1.94(2)Å and 2.149(7)Å, respectively. These result indicate that a volume of Co(1)O\(_6\) octahedron is smaller than that of Co(2)O\(_6\) octahedron, suggesting the Co(1) should be Co\(^{3+}\) and Co(2) be Co\(^{2+}\). In the

\[
\begin{array}{cccccc}
\hline
\# & x & y & z & B \\
\hline
Co(1) & 1 & 0 & 0 & 0 & 0.85(11) \\
Co(2) & 1 & 0.5 & 0.5 & 0 & 0.85(14) \\
O(1) & 1 & 0.245(5) & 0.247(4) & 0 & 0.78(6) \\
O(2) & 1 & 0.751(5) & 0.747(4) & 0 & 0.78(6) \\
O(3) & 1 & -0.033(4) & 0 & 0.163(5) & 0.78(6) \\
O(4) & 1 & 0.183(4) & 0.173(6) & 0 & 0.78(6) \\
O(5) & 0.060(4) & 0.25 & 0.25 & 0.25 & 0.78(6) \\
O(6) & 0.060(4) & 0.25 & 0.25 & 0.25 & 0.78(6) \\
La_{1.5}Ca_{0.5}CoO_4 & 1 & 0.000(1) & 0 & 0.3623(7) & 0.38(8) \\
La_{1.5}Ca(2) & 1 & 0.597(5) & 0.5 & 0.3602(7) & 0.38(6) \\
\hline
\end{array}
\]

\(A2mm\), \(R_{wp}=6.56\), \(S=1.78\)

\(a=5.4357(26)\) Å, \(b=5.4304(25)\) Å, \(c=12.3731(59)\) Å
previous crystal structure study of $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ [6], we also observed similar tendency of bond length change and determined Co(1) site as Co$^{3+}$ by using resonant x-ray diffraction. Therefore, we concluded that Co(1) is Co$^{3+}$ in Cr doped sample. In order to confirm that Cr is selectively occupied at Co(1) site, we compared the structural parameters. The structural parameters correspond to Co$^{2+}$ do not change within error, while O(3)-Co(1)-O(3) angle clearly change from 174.8(4)$^\circ$ to 169.9(4)$^\circ$. This result supports that Cr atoms selectively occupies the Co(1) site first.

In order to understand the spin fluctuation Cr doped system, we performed on the inelastic scattering in this system. Figure 3 shows inelastic neutron-scattering spectra for various energies at $T=15\text{K}$ in Cr doping sample. At 4meV magnetic excitation appears at commensurate position. It stars to split around 8meV and spin wave is seen up to 16meV. Spin dispersion of this system is almost as same as that of $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ [7]. Figure 4 shows the energy-Q slice showing around magnetic zone center. It reveals an energy gap of ~5meV in the magnetic spectrum. In $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ this gap feature also appear at 3meV and the magnetic dynamics is completely uncorrelated along the c-axis above 4meV [8]. This implies that the spectrum can be considered as three dimensional below this gap. Comparing the gap energy of these system, we concluded that the charge and spin orderings can be stabilized by tiny Cr doping.

First, we discuss about drastic enhancement of the out of plane correlation length. In $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$, two types of magnetic structure that correspond to the difference of spin stacking along $c$ direction are realized. On the other hand, two magnetic domains change to single domain by magnetic impurity doping. It’s expected to enhance the correlation length of the out of plane because of suppression of stacking fault along $c$ direction. However, checkerboard charge ordering is degraded in Fe and Mn cases. As a result, spin correlation is also degraded in these cases. As for the Cr doped case, charge ordering is not degraded because of selective replacement of Cr atoms. Therefore, drastic enhancement of correlation length along $c$-axis is realized.

Next, we consider the drastic change of magnetic structure by tiny magnetic impurity doping. One possible scenario for explaining the impurity effect is hole doping effect by excess oxygen. In this case, it expects that all impurity doped samples show magnetic reflections at $L=\text{integer}$ position because magnetic peaks at $L=\text{integer}$ were observed above $x=0.5$ in Ca doped sample. However, magnetic reflections at $L=\text{half-integer}$ were observed in Cr and Mn doped sample. It means hole doping is not major effect for changing magnetic structure. Another parameter to explain this effect is $c$-axis. Ca doping changes not only hole concentration but also lattice constant. If we focus on the $c$-axis, magnetic structure changes from $L=\text{integer}$ to $L=\text{half-integer}$ by increasing $c$-axis. In Mn and Cr doping case, it should be observed at $L=\text{half-integer}$ because $c$-axis increases by doping. However,
enhancement of c-axis was only about 0.5%. Therefore, it is more appropriate to consider another parameter causing the drastic change of magnetic structure in this system. We propose that Co$^{3+}$ spin is one plausible parameter to understand this impurity effect because Cr doping introduces not only excess oxygen but also distortion of octahedron around Co$^{3+}$. Indeed, magnetic peaks and excitation can be explained by Co$^{2+}$ spins. However, the strongest exchange interaction $J$ occurs through superexchange along straight bonds Co$^{2+}$-O-Co$^{3+}$-O-Co$^{2+}$, suggesting degrees of Co$^{3+}$ is also important for magnetic structure. To clarify the clues, magnetic impurity effect of local structure and inelastic neutron experiments at high energy region are now in progress by our group.

4. References

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