Charge and orbital ordered states in $Nd_{1-x}Sr_{1+x}MnO_4$ ($x = 0.67, 0.75$)

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Abstract

The charge and orbital ordered states in the single-layered manganite crystals, $Nd_{1-x}Sr_{1+x}MnO_4$ ($x = 0.67, 0.75$), have been investigated. We have observed the superlattice spots with modulation wave vector, $q = (\delta, \delta, 0)$, $\delta = \frac{1}{8}, \frac{1}{4}$ [$\sim \frac{1}{6}, \frac{1}{3}$] in $x = 0.75$[0.67] by resonant and non-resonant x-ray scattering. These results show that not only the atomic displacement pattern but also the charge-orbital structure has the unit cell of $4\sqrt{2}a \times \sqrt{2}a \times c$ [$3\sqrt{2}a \times \sqrt{2}a \times c$].

Key words: charge ordering; orbital ordering; resonant x-ray scattering;

1. Introduction

In the electric and magnetic properties of manganites, the charge, orbital and spin degrees of freedom each play important roles. The typical system, a layered-perovskite $La_{1-x}Sr_{1+x}MnO_4$, have intensively been studied so far [1]. For example, in $La_{0.5}Sr_{1.5}MnO_4$, the charge and orbital ordering affects the transport and the magnetic structure. These charge, orbital and spin ordered states were confirmed by the resonant x-ray scattering [2] and the neutron scattering [3]. However, the ordered states with $x > 0.5$ have seldom been investigated owing to the chemical phase separation [1]. By substituting Nd for La, Kimura *et al.* have recently succeeded in the growing the single crystals, $Nd_{1-x}Sr_{1+x}MnO_4$ ($0.67 \leq x \leq 1.0$) [4]. By an electron diffraction, they have found the superstructures for $x = 0.67, 0.75$ concerning with a steep rise of the resistivity. The superlattices observed here indicate only the atomic displacements which may induced by the charge-orbital ordering. To confirm the charge-orbital ordered states, we have studied the $Nd_{1-x}Sr_{1+x}MnO_4$ ($x = 0.67, 0.75$) using resonant and non-resonant x-ray scattering. We discuss the charge-orbital ordered state by comparing with Wigner-crystal and bi-stripe models in this paper.

2. Experimental results and discussions

X-ray scattering experiments were carried out at the beam lines 4C of the Photon Factory in KEK. The incident X-ray energy is about 6.55 keV of Mn K-edge and the energy resolution is about 2 eV. A four-circle diffractometer equipped with a closed cycle He cryostat was used. At room temperature, the crystal structure is space group $I4/mmm$ ($a = 3.82$, $c = 12.5$ Å for $x = 0.75$). All the indices are denoted in the $I4/mmm$ setting in this paper.

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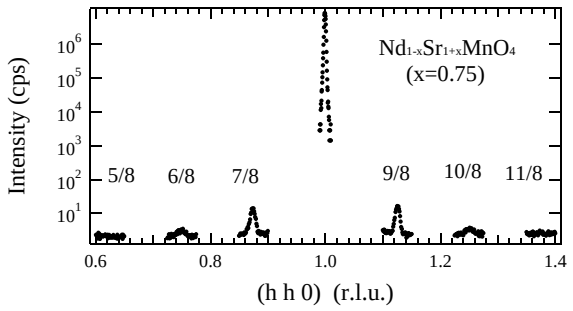

Fig. 1. (h h 0) scan at resonant energy for $x = 0.75$ at $T = 8$ K.

We have utilized resonant and non-resonant x-ray scattering. The resonant x-ray scattering is sensitive to charge-orbital ordered state, while the non-resonant x-ray scattering is caused by the atomic displacement. To determine the charge-orbital ordered states, we have searched the superlattice spots of the low temperature phase at Mn K-edge, $E = 6.555$ keV (a resonant energy). The scan along (h h 0) for $x = 0.75$ are presented in Fig. 1. Not only the modulation wave vector, $q = (\delta, \delta, 0)$, $\delta = \frac{1}{8}$, which was reported by the study of an electron diffraction [4], but also the weak signal at $\delta = \frac{1}{4}$ were observed. These signals observed at resonant energy may include non-resonant signals. The energy dependence of the scattering intensities has been measured at $(\frac{9}{8}, \frac{9}{8}, 0)$ and $(\frac{5}{4}, \frac{5}{4}, 0)$ so that the resonant signal can be discriminated from the non-resonant one. The energy spectrum at $(\frac{9}{8}, \frac{9}{8}, 0)$ shows a clear resonant feature, which is similar to the $LaMnO_3$ case [5], without the non-resonant signal. On the other hand, the energy dependence at $(\frac{5}{4}, \frac{5}{4}, 0)$ shows the interference process, involving the resonant and non resonant scattering. This non-resonant signal maybe attributed to the displacement of the oxygen atoms. In the superlattice spots $(2 \pm \delta, \pm\delta, 0)$ around the (2 0 0) reflection, the strong intensities of non-resonant scattering have been observed. We have observed no resonant intensity owing to the strong non-resonant scattering.

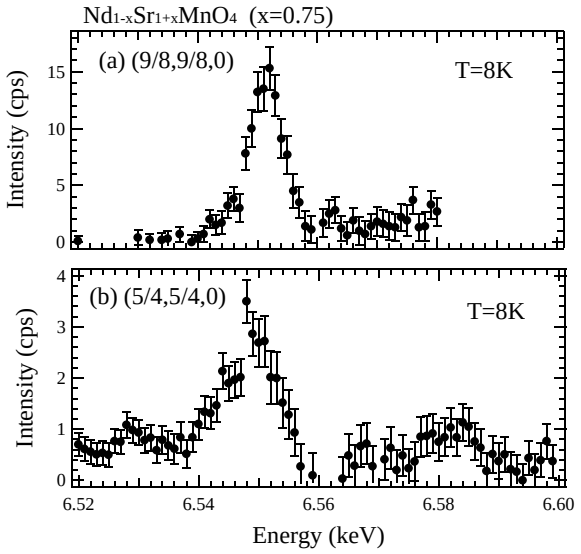

Fig. 2. Energy dependence of scattering intensities at (a) $(\frac{9}{8}, \frac{9}{8}, 0)$ and (b) $(\frac{5}{4}, \frac{5}{4}, 0)$.

The resonant and non-resonant scattering with $\delta = \frac{1}{8}, \frac{1}{4}$ indicates that the unit cell of the charge-orbital and atomic displacement pattern is $4\sqrt{2}a \times \sqrt{2}a \times c$ in the low temperature phase. The experimental results are examined by Wigner-crystal [6] and bi-stripe models [7]. However, these models can not explain the intensity ratio among the superlattice intensities. It would rather indicate the sinusoidal charge-orbital distribution along a-axis, which was discussed in ref. [8]

The same measurements for $x = 0.67$ have also been performed. The modulation wave vectors with $\delta \sim \frac{1}{6}, \frac{1}{3}$ have been observed by resonant and non-resonant scattering. We note that the superlattice intensity is much weaker than that for $x = 0.75$. The reason is still an open question.

In conclusion, we have studied the low temperature phase in $Nd_{1-x}Sr_{1+x}MnO_4$ ($x = 0.67, 0.75$) using resonant and non-resonant x-ray scattering technique. It has been elucidated that not only the atomic displacement but also the charge-orbital ordering have the superstructure of $\delta = \frac{1}{8}, \frac{1}{4}$ for $x = 0.75$ and $\delta = \frac{1}{6}, \frac{1}{3}$ for $x = 0.67$.

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