Charge and spin ordering in Nd$_{1/3}$Sr$_{2/3}$FeO$_3$

R. Kajimoto$^a$, Y. Oohara$^a$, M. Kubota$^a$, H. Yoshizawa$^a$, S. K. Park$^b$, Y. Taguchi$^b$, Y. Tokura$^b$

$^a$Neutron Scattering Laboratory, I. S. S. P., University of Tokyo, Tokai, Ibaraki, 319-1106, Japan

$^b$Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

We have investigated the charge and spin ordering in Nd$_{1/3}$Sr$_{2/3}$FeO$_3$ with neutron diffraction technique. This sample undergoes a charge ordering transition accompanying charge disproportionation of 2Fe$^{4+} \rightarrow$ Fe$^{3+} +$ Fe$^{5+}$. We measured the superlattice reflections due to the charge and spin ordering, and confirmed that charges and spins order simultaneously at $T_{CO} = 185$ K. The ordering pattern of charges and spins in this sample can be viewed as three dimensional stripe order, and is compared with two dimensional stripe order observed in other transition metal oxides.

**keywords:** A. oxides, B. crystal growth, C. neutron scattering, D. charge-density wave, magnetic structure

Charge ordering is widely seen in hole doped transition metal oxides, such as cuprates (e.g. La$_{2-x}$Sr$_x$CuO$_4$), nickelates (e.g. La$_{2-x}$Sr$_x$NiO$_{4-\delta}$) and manganites (e.g. Pr$_{1/2}$Ca$_{1/2}$MnO$_3$ and Nd$_{1/3}$Sr$_{2/3}$MnO$_3$). Because the charge ordering transition occurs at the region near the insulator-metal transition or superconducting transition, a number of works concentrated on the study of this phenomenon in order to clarify a key to understand the origin of the insulator-metal transition or superconducting transition. From these studies, it is widely recognized that the charge ordering phenomenon is a consequence of the coupling or the competition among the degrees of freedom of charge, spin, lattice, or orbitals.

Hole doped perovskite-type R$_{1/3}$Sr$_{2/3}$FeO$_3$ is one of the system which undergoes a charge ordering transition. In this system, the charge ordering accompanies charge disproportionation of 2Fe$^{4+} \rightarrow$ Fe$^{3+} +$ Fe$^{5+}$ and simultaneous antiferromagnetic spin ordering. A pioneering work with Mössbauer spectroscopy on La$_{1/3}$Sr$_{2/3}$Fe$_3$ by Takano et al. revealed that there are two kinds of Fe ions with the ratio of 2 : 1, and they were attributed to Fe$^{3+}$ and Fe$^{5+}$. This charge disproportionation state was confirmed by Battle et al. with the neutron powder diffraction measurements on the same compound. They observed the antiferromagnetic spin ordering with sixfold periodicity along the cubic [111] direction and showed that this magnetic structure was generated from the ordering of the layers of the Fe$^{3+}$ ions and the Fe$^{5+}$ ions along the cubic [111] direction in a sequence of ...Fe$^{3+}$Fe$^{3+}$Fe$^{5+}$... However, they could not observe the superlattice reflections due to the charge ordering presumably because of the weak intensity of the reflections in the powder sample, although it is well known that in many charge ordered systems the ordering of charges strongly couples with lattice and produces periodic modulation in the crystal structure.

Recently Li et al. observed the superlattice reflections of the charge ordering in La$_{1-x}$Sr$_x$FeO$_3$ single crystals for the first time by electron diffraction measurements. Park et al. showed that similar charge and spin ordering also exists in R$_{1/3}$Sr$_{2/3}$FeO$_3$ single crystals where R is rare-earth atoms other than La.

Neutron diffraction is very useful to investigated the spin and charge coupled physics such as charge ordering, because it can detect the direct evidence of the magnetic ordering and the structural modulations related to the ordering of charges which is formed in a bulk sample. Therefore we performed the neutron diffraction experiments on one of the 2/3-hole doped Fe oxides, Nd$_{1/3}$Sr$_{2/3}$FeO$_3$. By utilizing a single crystal sample, we could find the superlattice reflections due to the structural modulations by the charge ordering together with magnetic reflections. We could also detect a subtle change of the nature of the charge ordering as a function of temperature.

A single crystal sample studied in the present study was grown by the floating zone method in oxygen atmosphere with a traveling speed of 1.0 mm/h. The detailed procedures of the sample preparation have already been described elsewhere. The quality of the sample was checked by x-ray powder diffraction measurements and by electron probe microanalysis.

Neutron diffraction experiments were performed using triple axis spectrometer GPTAS installed at the JRR-3M reactor in JAERI, Tokai, Japan with fixed incident neutron momentums $k_i = 2.66$ Å$^{-1}$ and 3.83 Å$^{-1}$. The combination of collimators were 20'-40'-20'-open and 40'-80'-80'-80' (from monochromator to detector). Although the crystal structure of the sample has a slight rhombohedral distortion along the cubic [111] direction ($\alpha = 60.1^{\circ}$ at 300 K), we employed the cubic lattice ($\alpha \sim 3.85$ Å) notation of the scattering plane. The sample was mounted in an Al can filled with He gas, and was attached to the cold head of a closed-cycle helium gas refrigerator. The temperature was controlled within an accuracy of 0.2 K.

First we show the results of resistivity and magnetization measurements which were performed on the same crystal used in the neutron diffraction study. Figure 1 shows the temperature dependence of the resistivity and the spontaneous magnetization. The resistivity at room temperature is relatively low and gradually increases as temperature decreases. However, it shows a steep increase below $T_{CO}$ = 185 K because of the charge ordering transition. As shown in Fig. 1, small sponta-
neous magnetization appears below $T_{CO}$, signaling the onset of the antiferromagnetic ordering with minute spin canting.

In order to characterize the charge and spin ordering, we surveyed the (hhl) scattering plane and found some superlattice reflections below $T_{CO}$. For an example of such survey scans, we show in Fig. 2 profiles of line scans along [111] direction measured at 200 K and 10 K. One can see that at 10 K superlattice reflections appear at $(\frac{5}{6}, \frac{5}{6}, \frac{1}{6})$, $(\frac{5}{6}, \frac{1}{6}, \frac{5}{6})$, $(\frac{1}{6}, \frac{5}{6}, \frac{5}{6})$, $(\frac{2}{3}, \frac{2}{3}, \frac{1}{3})$, and $(\frac{5}{6}, \frac{5}{6}, \frac{1}{6})$. The observed superlattice reflections can be classified into three groups according to their modulation vectors $q$: $q_{+} = a^{*}(\frac{1}{6}, \frac{5}{6}, \frac{1}{6})$, $q_{-} = a^{*}(\frac{2}{3}, \frac{2}{3}, \frac{1}{3})$, and $q_{\perp} = a^{*}(\frac{1}{6}, \frac{1}{6}, \frac{5}{6})$. Due to the twin domains of the cubic structure, we also observed reflections with $q = a^{*}(\frac{1}{6}, \frac{1}{6}, \frac{1}{6})$ etc. in the (hhl) zone.

In order to analyze the magnetic moments for two Fe sites, we have performed neutron powder diffraction measurements to avoid difficulty in analyzing the single crystal caused by the domain distribution. The measurement was performed at 50 K, because below that temperature, the reflections by the ordering of the magnetic moments of Nd$^{3+}$ ions superpose the $q_{\perp}$ magnetic reflections (see below). The obtained value of the magnetic moments are $3.7 \mu_B$ for Fe$^{3+}$ site and $2.3 \mu_B$ for Fe$^{5+}$ site assuming the spins lie in the (111) plane. The direction of the spins in the (111) plane could not be determined due to the high symmetry. These values are similar to those obtained for La$_{1/3}$Sr$_{2/3}$FeO$_3$ (3.61 $\mu_B$ for Fe$^{3+}$ site and 2.72 $\mu_B$ for Fe$^{5+}$ site). The smaller observed magnetic moments than their nominal values of 5 $\mu_B$ and 3 $\mu_B$ indicate the strong hybridization of the Fe 3d orbitals and the O 2d orbitals because of the small charge-transfer energy of Fe oxides.

Figure 3 shows temperature dependence of the intensity of (a) the $q_{+}$ charge superlattice reflection, (b) $q_{\perp}$ (open circles) and $q_{\perp}$ (closed circles) spin superlattice reflections. As decreasing temperature, all the reflection start to develop at the same temperature $T_{CO} = 185$ K, indicating that charges and spins order simultaneously, which is consistent with the resistivity and magnetization data shown in Fig. 1. The transition at $T_{CO}$ is first order with small hysteresis of $\sim 4$ K. The increase of the intensity of the $(\frac{5}{6}, \frac{5}{6}, \frac{1}{6})$ reflection below $T \sim 50$ K comes from the ordering of the spins of Nd$^{3+}$ ions.

![FIG. 1. Temperature dependence of resistivity and spontaneous magnetization for Nd$_{1/3}$Sr$_{2/3}$FeO$_3$.](image)

![FIG. 2. A profile of the line scan along the [111] direction at 200 K and 10 K. Shaded peaks represent the superlattice reflections due to the magnetic and charge ordering.](image)
orbitals. Nevertheless, from the fact that the charge or
to the hybridization of the Fe 3d orbitals and the O 2p
moments distribute continuously from site to site due
the holes may locate on oxygen sites and the magnetic
ation. Of course this interpretation is too na¨ ıve because
suggesting the enhancement of the charge disproportion-
anomaly at
anomaly at
FIG. 3. Temperature dependence of the intensity of the
spin and charge super lattice reflections. (a) Charge superlat-
tice reflection (44/3,1/4,4/3). (b) Spin superlattice reflection (1/2,2/1,2) (open circles) and (1/2,1/2) (closed circles).

The development of the charge ordering almost satu-
ates around T_s = 150 K. The character of the spin
ordering also changes at this temperature. The slope of
the curve for the q_s reflection becomes steeper below
T_s, while the growth of the q_s reflection is slightly sup-
pressed around T_s.

The anomaly in the spin superlattice reflections at T_s
can not be explained by the rotation of the spin orient-
tations. Because the scattering vectors of the two kinds
of the spin reflections shown in Fig. (b) are parallel,
the rotation of the spins should produce the same effect
on the intensity of both spin reflections. Therefore, the
anomaly at T_s should be attributed to the change of
the ratio of the two Fourier component of the spin density
wave at this temperature. If one assume the moments
are localized at Fe sites, this means that the moments
on Fe^{3+} sites increase while those on Fe^{5+} sites decrease,
suggesting the enhancement of the charge disproportion-
atiation. Of course this interpretation is too na¨ ıve because
the holes may locate on oxygen sites and the magnetic
moments distribute continuously from site to site due
to the hybridization of the Fe 3d orbitals and the O 2p
orbitals. Nevertheless, from the fact that the charge or-
dering almost saturates around T_s, one can say that the
change of the distribution of the magnetic moments are
 correlated with the charge ordering, and the nature of the
charge and the spin ordering changes when the charge ordering sufficiently develops. We should note that we
also observed the similar anomaly at T < T_{CO} in an-
other 2/3-hole-doped charge disproportionated Fe oxides
Pr_{1/3}Sr_{2/3}FeO_3 [13].

One of the most interesting phenomena in the charge
ordering transition in the hole-doped transition metal
oxides is stripe order, where the doped holes align to
form domain walls and spins order antiferromagnetically.
Most of the stripe ordering observed so far, e.g. in
La_{2−x}Sr_xCuO_4 [4] or La_{2−x}Sr_xNiO_4+δ [5,6], is two di-

The number of the nearest holes around a hole in a domain
wall becomes larger because the domain walls become
2 D. Therefore, the energy loss by the Coulomb repul-
sion between the holes may become larger as compared
to the 3 D stripe order. On the other hand, the number of
the nearest sites for the undoped region also becomes
larger because of the three dimensionality, which may in-
crease the energy gain by the superexchange interaction
between spins.

In order to verify the above scenario, the energy scale
of the Coulomb interaction and the superexchange interaction should be examined. We would like to note that by recent Hartree-Fock calculations, it has been shown that the 3D stripe ordering observed in Fe oxides can be well explained by the superexchange interaction \(^{[14]}\), which indicates the importance of the spin interaction for the formation of the stripe order.

In summary, we have investigated the charge and spin ordering in a \(\text{Nd}_{1/3}\text{Sr}_{2/3}\text{MnO}_3\) crystal using neutron diffraction technique. We measured the superlattice reflections due to the charge and spin ordering, and confirmed that charges and spins order simultaneously at \(T_{\text{CO}} = 185\) K. The character of the charge and spin ordering changes at 150 K when the charge ordering almost saturates. The pattern of the charge and spin ordering in this sample can be viewed as the 3D stripe order, and the transition may be driven by the spin-charge coupling.

This work was supported by a Grant-In-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan and by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

\[1\] J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, and S. Uchida, Nature (London) \textbf{375} (1995) 561.
\[2\] J. M. Tranquada, D. J. Buttrey, and V. Sachan, Phys. Rev. B \textbf{54} (1996) 12318; P. Wochner, J. M. Tranquada, D. J. Buttrey, and V. Sachan, Phys. Rev. B \textbf{57} (1998) 1066.
\[3\] H. Yoshizawa, T. Kakeshita, R. Kajimoto, T. Tanabe, T. Katsufuji, and Y. Tokura, Phys. Rev. B \textbf{61} (2000) R854.
\[4\] Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. \textbf{74} (1995) 5108.
\[5\] H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Science \textbf{270} (1995) 961.
\[6\] M. Takano and Y. Takeda, Bull. Inst. Chem. Res., Kyoto Univ. \textbf{61} (1983) 406.
\[7\] P. D. Battle, T. C. Gibb, and P. Lightfoot, J. Solid State Chem. \textbf{84} (1990) 271.
\[8\] J. Q. Li, Y. Matsui, S. K. Park, and Y. Tokura, Phys. Rev. Lett. \textbf{79} (1997) 297.
\[9\] S. K. Park, T. Ishikawa, Y. Tokura, J. Q. Li, and Y. Matsui, Phys. Rev. B \textbf{60} (1999) 10788.
\[10\] Y. Taguchi, S. K. Park, and Y. Tokura, unpublished.
\[11\] A. E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. Suga, N. Kimizuka, Y. Takeda, and M. Takano, Phys. Rev. B \textbf{45} (1992) 1561.
\[12\] J. Matsuno, T. Mizokawa, and A. Fujimori, K. Mamiya, Y. Takeda, S. Kawasaki, and M. Takano, Phys. Rev. B \textbf{60} (1999) 4605.
\[13\] Y. Oohara, M. Kubota, H. Yoshizawa, S. K. Park, and Y. Tokura, unpublished.
\[14\] T. Mizokawa and A. Fujimori, Phys. Rev. Lett. \textbf{80} (1998) 1320.
\[15\] O. Zachar, S. A. Kivelson, and V. J. Emery, Phys. Rev. B