Inelastic neutron scattering study of phonon anomalies in La$_{1.5}$Sr$_{0.5}$NiO$_4$

R Kajimoto$^1$, M Fujita$^2$, K Nakajima$^1$, K Ikeuchi$^3$, Y Inamura$^1$, MNakamura$^1$ and T Imasato$^4$

$^1$ J-PARC Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
$^2$ Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan
$^3$ Research Center for Neutron Science and Technology, Comprehensive Research Organization for Science and Society, Tokai, Ibaraki 319-1106, Japan
$^4$ Department of Physics, Tohoku University, Sendai, Miyagi 980-8578, Japan

E-mail: ryoiichi.kajimoto@j-parc.jp

Abstract. The high-energy phonons in La$_{1.5}$Sr$_{0.5}$NiO$_4$, in which the checkerboard charge ordering is formed, was investigated by the inelastic neutron scattering. We found that the longitudinal modes show strong anomalies compared with La$_2$NiO$_4$. We argue the similarity and difference in the phonon anomalies between the present sample and the preceding works of different compositions.

La$_{2-x}$Sr$_x$NiO$_4$ is isostructural to one of the typical cupurate superconductors La$_{2-x}$Sr$_x$CuO$_4$. When $x = 0$, the compound is an antiferromagnetic insulator, where $S = 1$ spins on Ni$^{2+}$ (3d$^8$) ions order antiferromagnetically. Similarly to the cuprates, one hole per Ni ion is introduced in the NiO$_2$ planes by the substitution of a La$^{3+}$ ion with a Sr$^{2+}$ ion. In the course of exploring the origin of the superconductivity in the cuprates, the role of phonons have been extensively studied, and it was revealed that the hole doping induces a strong anomaly in the Cu-O bond stretching mode [1]. The phonon anomaly was regarded as a result of the electron-lattice coupling associated with charge inhomogeneity in the CuO$_2$ planes [2]. In the nickelates, the electron-lattice coupling is considered to be larger than the cuprates, as the charge inhomogeneity appears in the more obvious form of static charge stripes along the direction diagonal to the Ni square lattice [3–6]. Then, phonons in the nickelates have been studied by inelastic neutron scattering (INS) to investigate whether the doped holes or charge stripes affect particularly the bond-stretching modes, which are the highest-energy longitudinal optical (LO) modes in this system. Pintschovius et al. reported that the LO modes in non-doped La$_2$NiO$_4$ show only weak dispersion at $\sim$85 meV [7]. However, they found that the LO mode propagating along the [100] direction is susceptible to the non-stoichiometry, and observed similar softening to the cuprates in La$_{1.9}$NiO$_{3.93}$ [7, 8]. A study on powder samples of La$_{2-x}$Sr$_x$NiO$_4$ by McQueeney et al. showed that the $\sim$85 meV band in the phonon density of states (DOS) splits into two sub-bands at $\sim$75 meV and $\sim$85 meV at $x \geq 1/3$ [9]. Tranquada et al. reported that in a single crystal of La$_{1.69}$Sr$_{0.31}$NiO$_4$, the LO mode along [100] shows the similar softening, while that along [110] shows a splitting of the same magnitude as the softening. However, the anomalies in the phonons are independent on the charge stripe wave vector in this compound, $q_{SO} = (0.31, 0.31, 0)$ [10].

In the present study, we performed an INS study of the high-energy phonons in a single
crystal of \( \text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4 \). The wave vector of the charge stripes is proportional to \( x \), and in this composition, the charge ordering results in a nearly checkerboard ordering of \( \text{Ni}^{2+} \) and \( \text{Ni}^{3+} \) sites: The checkerboard charge ordering with \( \mathbf{q}_{\text{CO}} = (1/2, 1/2, 0) \) is formed below \( \sim 480 \) K, and it is taken over by incommensurate charge order with \( \mathbf{q}_{\text{CO}} \sim (0.44, 0.44, 0) \) below \( \sim 180 \) K \( [6, 11] \). We found that the dispersions of the phonon modes in \( x = 0.5 \) show anomalies similar to those observed in the \( x = 0.31 \) compound. However, we also found some difference between the two compositions.

Single crystals of \( \text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4 \) were grown by the floating-zone method. The crystal structure is tetragonal with the space group \( 14/mmm \) \( [12] \). The lattice constants determined by powder x-ray diffraction are \( a = 3.814 \) Å and \( c = 12.74 \) Å. Four crystal rods, each of which is \( \sim 5 \) mm in diameter and \( \sim 30 \) mm in length, were assembled for the present work. The INS measurement was performed on the chopper spectrometer 4SEASONS at J-PARC \( [13] \). The incident energy was \( E_i = 111 \) meV with the energy resolution being 10 meV at the elastic scattering condition. We aligned the crystals so that the [001] axis is parallel to the incident beam and the [110] axis is in the horizontal plane. Due to this crystal orientation, the observed data may include the contributions from out-of-plane phonon modes. However, they are expected to be small, because the high-energy phonon modes observed in the current experiment arise mainly from in-plane polarized oxygen vibrations \( [7, 9] \). We converted the raw data taken at \( \sim 5 \) K to a histogram of the intensity proportional to the dynamical structure factor \( S(Q, h\omega) \), where \( Q \) and \( h\omega \) are momentum and energy transfers, using the software package Utsusemi \( [14] \). In contrast to the previous INS studies using triple-axis spectrometers \( [7, 8, 10] \), scanning \( Q_x = h\omega^* \), \( Q_y = Kb^* \), or \( h\omega \) simultaneously changes the value of \( Q_z = Lc^* \) in the present study using the chopper spectrometer. Actually, for example, \( (H, K) = (0, 0), (1, 0), (1, 1) \) correspond to \( (H, K, L) = (0, 0, 7.66), (1, 0, 8.48), (1, 1, 9.43) \) at \( h\omega = 85 \) meV, respectively. However, considering the layered structure of the sample, we ignore \( Q_z \) and express \( Q \) in terms of \( (H, K) \). Though this assumption is not strictly correct, it is supported by the weak \( Q_z \) dependence of the highest-energy modes throughout the Brillouin zone observed in \( \text{La}_{1.9}\text{NiO}_3.87 \) \( [8] \). Since the obtained intensity decreases as a function of \( h\omega \), we further divided the intensity by \( h\omega \) for clarity in a high \( h\omega \) region. To correct the \( h\omega \)-dependent background, we estimated it by fitting the background of the intensity in the region of \( 0.9 < H < 1.1 \) and \( -0.1 < K < 0.1 \) to a quadratic function of \( h\omega \), then subtracted it from the data.

First, to survey the overall structure of the high-energy phonons, we investigated a \( Q \) map of the neutron scattering intensity. Figure 1(a) shows the intensity map at \( h\omega = 85 \) meV on the \( H-K \) plane. This energy is almost equal to that of the bond-stretching mode in \( \text{La}_{2}\text{NiO}_4 \) \( [7] \). A characteristic intensity modulation is observed in Fig. 1, which reflects some dispersions of the high-energy modes. There are strong spots at \( (H, K) \) \( = (1, 1), (\pm 1, 0), \) and \( (0, \pm 1) \). In addition, the intensity shows streaks along the \( (H, \pm 1) \) and \( (\pm 1, K) \) lines. These spots and streaks suggest that the phonon mode along these lines shows a weak dispersion, while those along the other

**Figure 1.** (a) Intensity map of the excitations in \( \text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4 \) at \( \sim 5 \) K, which is cut at \( h\omega = 85 \pm 3 \) meV and displayed on the \( H-K \) plane. The intensity is smoothed by a Gaussian filter. (b) Directions in the \( H-K \) plane along which the data in figure 2 are shown (see caption of figure 2 and text).
Figure 2. Intensity map of the high-energy excitations in \( \text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4 \) at \( \sim 5 \) K on the \( Q-\hbar\omega \) planes. The intensity is smoothed by a Gaussian filter. Each data is sliced along each \( Q \) direction with a width of \( H \) or \( K = \pm 0.1 \). The directions of the \( Q \) axis of (a), (b), (c), and (d) are \( A + A', B + B', C + C', \) and \( D + D' \) in figure 1(b), respectively (see text). Circles indicate the energies of phonons observed in \( \text{La}_2\text{NiO}_4 \) [7].

The observed anomalies in the LO modes as well as their minimum energies at \( \sim 73 \) meV are apparently similar to those observed in \( x = 0.31 \) [10]. In \( x = 0.31 \), though the energy of the LO phonon along [100] continuously softens as a function of \( Q \), that along [110] shows a splitting into two modes. Moreover, the latter anomaly is independent on \( q_{\text{CO}} \). Tranquada \textit{et al.} interpreted the splitting of the LO mode is caused by the local breathing motion of O ions...
about the hole-doped Ni sites (Ni$^{3+}$ sites). The similarities between the phonon anomalies in $x = 0.5$ and those in $x = 0.31$ supports their idea that the doped holes cause local effects on the bond-stretching phonons independent on the hole concentration.

However, there is some difference between the two compounds. Contrary to $x = 0.31$, in $x = 0.5$, the dispersion of the LO mode along [110] shows a clear softening with its minimum at (0.5,0.5) [figure 2(b)], though there is very weak $Q$ independent intensity at $\sim 85$ meV. In other words, the softening behavior is superior to the splitting behavior along [110] in this compound. On the other hand, the splitting behavior is more clearly observed in the data along [100] [figure 2(a)]. The difference between the present $x = 0.5$ sample and $x = 0.31$ may be related to the difference in types of the charge ordering. In the case of the checkerboard charge ordering in $x = 0.5$, the holes enter every two Ni sites, and Ni$^{2+}$ sites and Ni$^{3+}$ sites always share the in-plane O ions. Therefore, the vibrations of the shared in-plane O ions may become more coherent along the direction of the charge-ordering wave vector, [110], resulting in the softening of the dispersion.

In conclusion, we performed an INS study on La$_{1.5}$Sr$_{0.5}$NiO$_4$ to investigate the effects of hole doping on the high-energy phonon modes. We found that the longitudinal modes show clearly different dispersions compared with La$_2$NiO$_4$, though the transverse modes are quite similar to those in La$_2$NiO$_4$. In particular, the longitudinal mode along the direction diagonal to the Ni square lattice shows a clear softening, in contrast to $x = 0.31$ where the mode shows a splitting [10]. We interpret the difference in the phonon anomalies between $x = 0.5$ and $x = 0.31$ as the difference in the type of charge ordering.

Acknowledgments
The experiment on 4SEASONS was conducted under the project numbers 2012I0100 and 2012I0101.

References
[1] Reznik D 2010 Advances in Condensed Matter Physics 2010 523549
[2] Reznik D, Pintschovius L, Ito M, Iikubo S, Sato M, Goka H, Fujita M, Yamada K, Gu G D and Tranquada J M 2006 Nature 440 1170
[3] Chen C H, Cleong S W and Cooper A S 1993 Phys. Rev. Lett. 71 2461
[4] Tranquada J M, Buttrey D J, Sachan V and Lorenzo J E 1994 Phys. Rev. Lett. 73 1003
[5] Tranquada J M, Buttrey D J and Sachan V 1996 Phys. Rev. B 54 12318
[6] Yoshizawa H, Kakeshita T, Kajimoto R, Tanabe T, Katsufuji T and Tokura Y 2000 Phys. Rev. B 61 R854
[7] Pintschovius L, Reichardt W, Braden M, Dhalenne G and Revcolevschi A 2001 Phys. Rev. B 64 094510
[8] Pintschovius L, Bassat J M, Odier P, Gervais F, Chevrier G, Reichardt W and Gompf F 1989 Phys. Rev. B 40 2229
[9] McQueeney R J, Sarrao J L and Osborn R 1998 Phys. Rev. B 60 80
[10] Tranquada J M, Nakajima K, Braden M, Pintschovius L and McQueeney R J 2002 Phys. Rev. Lett. 88 075505
[11] Kajimoto R, Ishizaka K, Yoshizawa H and Tokura Y 2003 Phys. Rev. B 67 014511
[12] Millburn J E, Green M A, Neumann D A and Rosseinsky M J 1999 J. Solid State Chem. 145 401
[13] Kajimoto R, Nakamura M, Inamura Y, Mizuno F, Nakajima K, Ohira-Kawamura S, Yokoo T, Nakatani T, Maruyama R, Soyama K, Shibata K, Suzuya K, Sato S, Aizawa K, Arai
M, Wakimoto S, Ishikado M, Shamoto S, Fujita M, Hiraka H, Ohoyama K, Yamada K and Lee C H 2010 *J. Phys. Soc. Jpn.* **80** SB025

[14] Inamura Y, Nakajima K, Kajimoto R, Nakatani T, Arai M, Otomo T, Suzuki J, So J Y and Park J G 2010 *Proc. 19th Meet. Int. Collaboration of Advanced Neutron Sources* (PSI-Proceedings 10-01)