Evidence for charge and spin order in single crystals of La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$

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Charge and spin order is intimately related to superconductivity in copper oxide superconductors. To elucidate the competing orders in various nickel oxide compounds are crucial given the fact that superconductivity has been discovered in Nd$_6$Sr$_{0.2}$NiO$_2$ films. Herein, we report structural, electronic transport, magnetic, and thermodynamic characterizations on single crystals of La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$. La$_3$Ni$_2$O$_7$ is metallic with mixed Ni$^{2+}$ and Ni$^{3+}$ valent states. Resistivity measurements yield two transition-like kinks at ∼110 and 153 K, respectively. The kink at 153 K is further revealed from magnetization and specific heat measurements, indicative of the formation of charge and spin order. La$_3$Ni$_2$O$_6$ single crystals obtained from topochemical reduction of La$_3$Ni$_2$O$_7$ are insulating and show an anomaly at ∼176 K on magnetic susceptibility. The transition-like behaviors of La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$ are analogous to the charge and spin order observed in La$_4$Ni$_2$O$_{10}$ and La$_4$Ni$_3$O$_8$, suggesting charge and spin order is a common feature in the ternary La-Ni-O system with mixed-valent states of nickel.

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I. INTRODUCTION

The recent discovery of superconductivity in Nd$_{0.8}$Sr$_{0.2}$NiO$_2$ films has aroused great research enthusiasm in the search for superconductivity and understanding the pairing mechanism in nickel oxide system$^{1}$. Particularly, whether the mechanisms of the superconductivity in nickelates and copper oxide superconductors are the same remaining an open question. The superconductivity, spin order, and charge order could be tuned by carrier doping in cuprates. It is widely accepted that the static and dynamic spin and charge orders play a crucial role in the mechanism of superconductivity.$^{2,3}$

The ternary nickel oxide Ln-Ni-O system (Ln = La, Pr, Nd, Sm, and Eu) contains the Ruddlesden-Popper (RP) compounds Ln$_{n+1}$Ni$_n$O$_{3n+1}$, which possess $n$ layers of perovskite-type LnNiO$_3$, separated by single rock-salt LnO$_2$ layer along the $c$ axis.$^{4-7}$ The Ni ions exhibit mixed valences of Ni$^{2+}$ (3$d^7$) and Ni$^{3+}$ (3$d^8$). By a topochemical reduction method, two apical oxygen atoms of a NiO$_6$ octahedra could be removed and the remained oxygen atoms rearrange and result in a fluorite Ln-O$_2$-Ln layer, as shown in Fig. 1. The topochemical reduced compounds Ln$_{n+1}$Ni$_n$O$_{3n+2}$ with mixed-valent states of Ni$^{2+}$ (3$d^8$) and Ni$^{3+}$ would form. The structures of the RP system and the PR reduced system are analogous to the ternary Ln-Cu-O system, especially the Ni-O planes that are regarded as alternative superconducting planes like the Cu-O planes in cuprates. Theorists suggested that superconductivity may be induced by doping low-spin Ni$^{3+}$ ($S = 0$) to a nickelate antiferromagnetic (AF) insulator with Ni$^{2+}$ ($S = 1/2$) in a square planar coordination with O ions.$^8$ This could be realized in the chemical reduced RP phase Ln$_{n+1}$Ni$_n$O$_{2n+2}$ by hole doping on the Ln site, such as Sr doped Ln$_{0.8}$Sr$_{0.2}$NiO$_2$, where Ln=La, Nd, and Sm. Superconductivity has been indeed observed in films of these hole doped compounds and Nd$_6$Ni$_5$O$_{12}$, where nickel ions exhibit an average valence of +1.$^{2,9,10}$ The transition temperature $T_c$ of the superconducting films could be enhanced by pressure$^{11}$. However, superconductivity has not been observed in bulk samples of the Ln-Ni-O system under ambient or high pressure.$^{6,12-14}$

Progress on studies of the charge and spin order has been made due to the availability of high-quality single crystals for the La-Ni-O system grown by the floating zone technique with high oxygen pressure. AF transitions were identified on metallic LaNiO$_3$ (n=∞) and La$_4$Ni$_3$O$_{10}$ (n=3) single crystals by neutron scattering

| $n$ | Ln$_{n+1}$Ni$_n$O$_{3n+1}$ composition Ni valence | Ln$_{n+1}$Ni$_n$O$_{3n+2}$ composition Ni valence |
|----|-----------------------------------|-----------------------------------|
| ∞  | 113                               | +3                                |
| 3  | 4310                              | +2.67                             |
| 2  | 327                               | +2.5                              |
| 1  | 214                               | +2                                |

TABLE I: Empirical formula, corresponding $n$, and the average Ni valence of the RP phases Ln$_{n+1}$Ni$_n$O$_{3n+1}$ and the chemical reduced phases Ln$_{n+1}$Ni$_n$O$_{2n+2}$, Ln = La, Pr, Nd, Sm, and Eu.
studies, which were absent for previous measurements on powder samples. The AF transition has been ascribed to spin density wave (SDW) that originates from Fermi surface nesting, differing from the spin order in doped \( n = 1 \) \( \text{La}_{2-x}\text{Sr}_{x}\text{NiO}_4 \) and cuprates. A charge density wave (CDW) coincident with the SDW was found in \( \text{La}_3\text{Ni}_2\text{O}_6 \) and was suggested to result in a metal-to-insulator transition. For the topochemically reduced product \( \text{La}_3\text{Ni}_2\text{O}_8 \), synchrotron X-ray and neutron diffraction also reveal stacked charge and spin stripe weakly correlated along the \( c \) axis. In this case, \( \text{La}_3\text{Ni}_2\text{O}_8 \) is an insulator and the charge and spin order results from the competition between the Coulomb repulsion, spin orbital coupling, and magnetic exchange interaction.

The \( n=2 \) RP compound \( \text{La}_3\text{Ni}_2\text{O}_7 \) and chemical reduced product \( \text{La}_3\text{Ni}_2\text{O}_6 \) consisting of the bilayer \( \text{NiO}_2 \) planes are analogous to the trilayer \( \text{La}_4\text{Ni}_3\text{O}_{10} \) and \( \text{La}_4\text{Ni}_3\text{O}_8 \) in structural and physical properties. Theoretical calculations for \( \text{La}_3\text{Ni}_2\text{O}_7 \) and \( \text{La}_4\text{Ni}_3\text{O}_{10} \) suggest existence of a hidden one-dimensional Fermi surface nesting which would result in CDW instability. For \( \text{La}_3\text{Ni}_2\text{O}_6 \) and \( \text{La}_4\text{Ni}_3\text{O}_8 \), charge-ordered related structural distortion and magnetic order will emerge in the ground state. The electronic density of states of \( \text{La}_3\text{Ni}_2\text{O}_7 \) indeed has an abrupt change at around 100–120 K, reflected in both the Hall coefficient and Seebeck coefficient. However, neutron diffraction, resistivity, and magnetic susceptibility measurements on powder samples of \( \text{La}_3\text{Ni}_2\text{O}_7 \) that were synthesized through the soft chemical method did not reveal evidence of charge or spin order. \( \text{La}_3\text{Ni}_2\text{O}_6 \) has raised great interest because of the similarities of the electronic structures to cuprates and possible superconductivity through tuning the valence by carrier doping or high pressure. Moreover, NMR study of \( \text{La}_3\text{Ni}_2\text{O}_6 \) suggests the existence of magnetic interactions, but the basic magnetic properties are still not clear. As a matter of fact, a comprehensive study of \( \text{La}_3\text{Ni}_2\text{O}_7 \) and \( \text{La}_3\text{Ni}_2\text{O}_6 \) is lacking due to the unavailability of single crystals. Single crystal growth of the samples with the average valences of nickel ions larger than +2 requires high pressure oxygen and the pressure window is narrow for a specific compound. However, single crystals are crucial for investigations of the possible emerging orders of charge and spin in \( \text{La}_3\text{Ni}_2\text{O}_7 \) and \( \text{La}_3\text{Ni}_2\text{O}_6 \) in order to ascertain the universality for the ternary nickel oxide system, and pave a way for further manipulation of the states of nickel, even for realization of superconductivity.

Here, we report successful growth of \( \text{La}_3\text{Ni}_2\text{O}_7 \) single crystals by a high oxygen pressure floating zone technique and the achievement of \( \text{La}_3\text{Ni}_2\text{O}_8 \) single crystals through a subsequent low temperature topochemical reduction method. Electrical resistivity measurements on the single crystals of \( \text{La}_3\text{Ni}_2\text{O}_7 \) and \( \text{La}_3\text{Ni}_2\text{O}_6 \) show significantly different properties. \( \text{La}_3\text{Ni}_2\text{O}_7 \) is metallic while \( \text{La}_3\text{Ni}_2\text{O}_6 \) is insulating. Superconductivity has not been realized in \( \text{La}_3\text{Ni}_2\text{O}_6 \) under pressure up to 25.3 GPa. Anomalies in resistivity, susceptibility, and specific heat that may correspond to spin and charge order have been observed in both compounds. The results indicate the emergent order of charge and spin is universal for the nickelates with mixed-valent states of nickel.

II. EXPERIMENTAL METHODS

Polycrystalline samples were synthesized through the standard solid-state reaction techniques. Stoichiometric amounts of \( \text{La}_2\text{O}_3 \) and an excess of 0.5% \( \text{NiO} \) (Macklin, 99.99%) were thoroughly ground. The excess of 0.5% NiO was used to compensate the loss of volatilization. The ground mixtures were made into pellets and sintered at 1100 °C for 50 h. After cooling down to room temperature, the reactants were reground and made into pellets for sintering again. The procedures were repeated for 3 times to ensure a complete and homogeneous reaction. The seed and feed rods were prepared by pressing the powders under hydrostatic pressure and sintered at 1400 °C for 12 h. The rods were approximate 9 cm in length and 0.6 cm in diameter.

High oxygen pressure is crucial for synthesis of the homologous RP system of nickelates. A vertical optical-image floating-zone furnace designed for a 100 bar high pressure (HKZ, SciDre, Dresden) was employed in our single crystal growth. \( \text{La}_3\text{Ni}_2\text{O}_7 \) single crystals were grown with an oxygen pressure at \( p(\text{O}_2) = 15 \) bar and a 5 kW Xenon arc lamp. The traveling rate was 3 mm/h after a fast traveling procedure at 10 mm/h to improve the density. After that, the feed and seed rods counter-rotate at 15 and 10 rpm, respectively, in order to improve homogeneity. \( \text{La}_3\text{Ni}_2\text{O}_6 \) was obtained from the \( \text{La}_3\text{Ni}_2\text{O}_7 \) single crystals by the topochemical reduction method. \( \text{La}_3\text{Ni}_2\text{O}_7 \) single crystals were enclosed in an aluminum foil and sealed in vacuum with stoichiometric \( \text{CaH}_2 \) powders. The reaction was under the condition of 300 °C for 4 days.

X-ray photoemission spectroscopy (XPS) measurements was carried out on an XPS machine (Escalab 250 Xi, Thermo Fisher). Argon sputtering was adopted to remove the surface contamination. The sputtering depth was about 100 nm. The monochromatic Al Kα radiation with photon energy of 1486.6 eV was applied to analyses the valent states of nickel. The X-ray beam was focused on a 0.5 mm spot surface. In order to obtain high-resolution spectra, the electron energy analyzer was operated at a pass energy of 30 eV. The C 1s photoelectron line (284.8 eV) was used to calibrate the binding energies of the photoelectrons.

Magnetic susceptibility, resistivity, and specific heat measurements were performed on a physical property measurement system (PPMS, Quantum Design). In situ high-pressure electrical resistance measurements were carried out in a diamond anvil cell made from a Be-Cu alloy using a standard four-probe technique. NaCl powders were employed as the pressure transmitting medium. The pressure in the resistance measurements
was calibrated by the ruby fluorescence shift at room temperature. X-ray single crystal diffraction (XRD) was performed on a single-crystal X-ray diffractometer (SuperNova, Rigaku) using the Mo-Kα radiation at 300 K. The diffraction data were refined by the Rietveld method. Energy-dispersive X-ray spectroscopy (EDS) (EVO, Zeiss) was employed to determine the compositions of the crystals. In addition, Laue X-ray diffraction technique was utilized to confirm the crystal orientation and single crystallinity.

III. RESULTS

A. La$_3$Ni$_2$O$_7$

Crystal structures of La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$ are shown in Fig. 1(a). La$_3$Ni$_2$O$_7$ crystallizes in orthorhombic symmetry (space group: Cmcm) with distorted vertex-sharing NiO$_6$ octahedra and rock-salt La-O layers. The structure can be termed as inter-growth octahedra and rock-salt La-O layers. The structure is stacked by two corner-sharing square NiO$_2$ planes and a La-O fluorite-type layer along the c direction. La$_3$Ni$_2$O$_6$ with the apical oxygen atoms removed crystallizes in tetragonal symmetry (space group: I$_4$/mmm). The structure is preserved in the fitting of the two main peaks for Ni$^{2+}$ in (b). Figure 2(a) shows the XPS spectrum of Ni ions in La$_3$Ni$_2$O$_7$. As a comparison, an XPS spectrum of Ni$^{2+}$ measured on NiO is presented in Fig. 2(b). The main peaks of the spectrum of Ni$^{2+}$ locate at 853.6 and 855.6 eV. In addition, a broad satellite peak appears at a higher binding energy of 860.8 eV. These features are typical for nickel ions with the divalent oxidation state. The XPS spectrum of La$_3$Ni$_2$O$_7$ exhibits asymmetric doublet peaks at 853.0 and 855.7 eV as shown in Fig. 2(a). We preserve the ratio of the two peaks of Ni$^{2+}$ as measured on NiO and fit the spectrum of La$_3$Ni$_2$O$_7$. A peak at 855.7 eV could be separated, yielding the existence of the trivalent oxidation state. Thus, our XPS measurements reveal that the valent states of nickel in La$_3$Ni$_2$O$_7$ are a mixture of the divalent Ni$^{2+}$ and trivalent Ni$^{3+}$ oxidation states.

Figure 3(a) shows the temperature dependence of the resistance for La$_3$Ni$_2$O$_7$ single crystals, revealing a metallic ground state that is analogous to the $n = 3$, and $\infty$ RP compounds. We observe two anomalies in resistance, one at $\sim$110 K and the other one at 153 K. They could be identified unambiguously in the deviation of resistance against temperature $dR/dT$ as shown in Fig. 3.

![FIG. 1: (a) Sketches of the crystal structures of La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$. A photo of the single crystal of La$_3$Ni$_2$O$_7$. (b) X-ray diffraction patterns integrated from single crystal diffraction on La$_3$Ni$_2$O$_7$ and (c) La$_3$Ni$_2$O$_6$. The insets in (b) and (c) are diffraction patterns in reciprocal space corresponding single crystals collected on a single crystal X-ray diffractometer.](image1)

![FIG. 2: (a) XPS measurements of the Ni 2p core levels for La$_3$Ni$_2$O$_7$ and (b) NiO. The pink areas and satellites 1 and 2 in (b) are deconvoluted of the Ni 2p$_{3/2}$ XPS data. The ratio of the two main peaks for Ni$^{2+}$ are preserved in the fitting of the Ni 2p core levels for La$_3$Ni$_2$O$_7$ in (a). The black solid lines are the experimental data. The red line is a fitting of the total intensities.](image2)
TABLE II: Structural parameters for single crystals of La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$ at 300 K measured with the Mo K$_\alpha$ radiation with $\lambda = 0.7107$ Å. The data were collected in the range of $1.17^\circ \leq 2\theta \leq 40.84^\circ$.

| Empirical formula | La$_3$Ni$_2$O$_7$ | La$_3$Ni$_2$O$_6$ |
|-------------------|-------------------|-------------------|
| Space group       | Cmcm (Orthorhombic)| 14/mmm (Tetragonal)|
| Unit-cell parameters | $a = 5.4000(7)$ Å; $b = 5.4384(7)$ Å | $a = 3.9720(4)$ Å; $c = 19.3684(4)$ Å |
|                   | $c = 20.4554(4)$ Å | $\alpha = 60^\circ$; $\beta = 90^\circ$; $\gamma = 90^\circ$ |
| La1               | (0.32, 0.75, 0.25) | (1.1, 0.5) |
| La2               | (0.5, 0.25, 0.75)  | (1, 0.32) |
| Ni                | (0.40, 0.75, 0.75) | (0.5, 0.5, 0.42) |
| O1                | (0.41, 1, 1)      | (1.0, 0.42) |
| O2                | (0.5, 0.71, 0.75) | (0.5, 0.025) |
| O3                | (0.40, 0.5, 0.5)  | -- |
| O4                | (0.30, 0.78, 0.75) | -- |
| Goodness-of-fit on $F^2$ | 1.184             | 0.966             |
| Final $R$ indexes (all data) | $R_1=0.0327$         | $R_1=0.0469$ |

FIG. 3: (a) The red and black lines are resistance of two La$_3$Ni$_2$O$_7$ single crystals as a function of temperature. The blue line is a derivative of the resistance in red. (b) Temperature dependence of the total specific heat of La$_3$Ni$_2$O$_7$. The dashed line is a fitting to the formula described in the text. The inset shows an abnormal change at 153 K. (c) Magnetization of La$_3$Ni$_2$O$_7$ measured with a magnetic field of $\mu_0 H = 0.4$ T parallel to and perpendicular with the c axis under zero-field cooled condition. The red lines show derivatives of the magnetization in arbitrary units. (d) Magnetization against the magnetic field $\mu_0 H$ for $H \parallel c$ and $H \perp c$ at 100, and 300 K.

(a). The former one at $\sim 110$ K is close to the anomalies observed in Hall and Seebeck coefficients$^{20,22,23}$. While the later one at 153 K is weaker and has not been identified in the previous measurements on powder samples. For LaNiO$_3$ and La$_4$Ni$_3$O$_{10}$, a metal-metal transition near 150 K has been observed in resistivity, where the origin has been proved to result from intertwined charge and spin density wave$^{15,16}$.

To investigate the origin of the transitions in La$_3$Ni$_2$O$_7$, we measured the specific heat and magnetization against temperature and magnetic field. The specific heat for temperatures between 3 and 200 K is shown in Fig. 3 (b). A model $C = \gamma T + C_{ph}$ was employed to fit the data, where $\gamma T$ and $C_{ph}$ represent the contributions of electrons and phonons, respectively. A modified Debye model considering the existence of two phonon modes that reconcile the heavy atoms (La and Ni) and light atoms (O) was considered to describe the phonon contribution, $C_{ph} = 9R \sum_{n=1}^{2} C_n \frac{T}{\theta_{Dn}} \int_{0}^{\theta_{Dn}/T} x^4 e^x dx$, where $R = 8.314$ Jmol$^{-1}$K$^{-1}$ is the ideal gas constant and $C_n$ represents the numbers of the heavy or light atoms in a formula unit. The modeling reveals that, of the 12 atoms in the formula unit, 5 atoms have a Debye temperature $\theta_{D1}$ of 298 $\pm$ 3 K and 7 atoms have a Debye temperature $\theta_{D2}$ of 620 $\pm$ 4 K$^{41,42}$. The fitting also yields $\gamma = 7.3$ mJmol$^{-1}$K$^{-2}$, close to the value of 6.4 mJmol$^{-1}$K$^{-2}$ revealed from powder samples$^{26}$. With the estimated densities of charge-carriers and mass of the free-electrons, the value of electron effective mass $m^*/m_0$ of La$_3$Ni$_2$O$_7$ is $\approx 2.12$, reminiscent of 2.56 for La$_3$Ni$_3$O$_{10}$ and much lower than 15 for LaNiO$_3$.$^{20,25,43}$ The effective mass of electrons suggests that the electronic correlations in La$_3$Ni$_2$O$_7$ and La$_4$Ni$_3$O$_{10}$ are weaker than that of the $n=\infty$ compound LaNiO$_3$. The anomaly at 153 K could also be observed in specific heat, as shown in the inset of Fig. 3 (b), in consistence with the temperature of the anomaly at 153 K in resistance.

Figure 3 (c) displays temperature dependence of the magnetization of La$_3$Ni$_2$O$_7$ single crystals at 4000 Oe. The kink at $\sim$153 K for both $H \parallel c$ and $H \perp c$ could be identified in magnetization and $d\chi/dT$, suggesting a same physical origin as the anomalies at the identical temperature in resistance and specific heat. While the anomaly at $\sim$110 K in resistance does not show in magnetization. The upturn below 50 K with decreasing temperature in Fig. 3 (c) may be related to magnetic impurities or lattice imperfections. We note the magnetization of La$_3$Ni$_2$O$_7$ single crystals shown in Fig. 3 (c) is reminiscent of that observed in LaNiO$_3$ and La$_4$Ni$_3$O$_{10}$ single crystals$^{15,16}$. 

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For the later two materials, intertwined charge and spin density wave has been confirmed by neutron and X-ray diffraction measurements. The magnetization as a function of magnetic field and temperature is shown in Fig. 3 (d). The magnetization evolves linearly against magnetic field up to $\mu_0 H = 10$ T, indicating antiferromagnetic correlations. In the scenario of spin order, the anisotropy of the magnetization in Fig. 3 (d) suggests the moment of Ni aligned in-plane.

B. La$_3$Ni$_2$O$_6$

The ground state of La$_3$Ni$_2$O$_6$ with mixed Ni$^{3+}$d$^0$ ($S = 1/2$) and Ni$^{2+}$d$^6$ ($S = 0$) was predicted to be an AF insulator with a checkerboard charge order and both the AF and ferromagnetic (FM) interactions. Pressure will suppress the FM interactions further and may induce superconductivity. However, only was the insulating state confirmed due to the limitation of powder samples. We obtain single crystals of La$_3$Ni$_2$O$_6$ from topochemical reduction of the La$_3$Ni$_2$O$_7$ single crystals. Temperature dependence of the electrical resistivity $\rho$ is shown in Fig. 4 (a) and the inset. The semiconducting behavior is analogous to the measurements on powder samples. The resistivity of La$_3$Ni$_2$O$_6$ displays a weak kink at 101 K. In contrast to the abrupt change in resistivity at $\sim 100$ K for La$_4$Ni$_3$O$_7$ that corresponds to the formation of charge and spin stripe order.

By fitting the resistivity to the activation-energy model $\rho(T) = \rho_0 \exp(E_a/k_BT)$, two thermal activation energy gaps of $E_a = 54$ and 100 meV are obtained, corresponding to $84 \leq T \leq 125$ K and $176 \leq T \leq 300$ K, respectively. To explore superconductivity in La$_3$Ni$_2$O$_6$, the resistance measured under pressure is shown in Fig. 4 (b). The metallization is achieved at 6.1 GPa. However, no superconductivity emerges in our samples up to 25.3 GPa.

Figure 4 (c) displays the magnetization of La$_3$Ni$_2$O$_6$ with the magnetic field perpendicular to the $c$ axis. A kink at $\sim 176$ K could be identified in the derivative of magnetization for the magnetic fields at 1 and 2 T. As theoretical suggestions, the kink on magnetization at 176 K may be associated with the charge and spin order of La$_3$Ni$_2$O$_6$, which may also result in the change of the fitted thermal activation gaps against temperature as shown in the inset of Fig. 4 (a). The magnetization decreases as the temperature increasing, similar to the behavior of a ferromagnet. It is known that the topochemical reduction method would induce Ni impurity. A high-temperature magnetization measurement was conducted, revealing a FM transition at $T_c = 630$ K, as shown in Fig. 4 (d). The result demonstrates the existence of Ni impurity.

IV. DISCUSSION AND SUMMARY

The mixed-valent and spin states of Ni in the ternary La-Ni-O system tend to form charge and spin order. The emergence of the two types of order has been verified in hole doped La$_{2-x}$Sr$_x$NiO$_4$ ($x = 1/4$, 1/3, and 1/2), La$_4$Ni$_3$O$_{10}$, and La$_4$Ni$_3$O$_8$. For the trilayer RP compounds, the ratio of the magnetic Ni$^{3+}$ ($S = 1/2$) and nonmagnetic Ni$^{2+}$ ($S = 0$) is 2 : 1; for the bilayer RP compounds, the value of this ratio drops to 1 : 1. The formation of charge order is expected, while the spin order may be weaker in the bilayer compounds. The changes in resistivity, susceptibility, and specific heat at 153 K are indeed less pronounced in La$_3$Ni$_2$O$_6$ single crystals compared to that of La$_4$Ni$_3$O$_{10}$. The possibility that the charge order emerges in the bilayer La-Ni-O system without accompanying by the spin order could not be ruled out. In this case, the anomaly in magnetization could be due to charge-spin interactions. Our Raman scattering measurements on La$_3$Ni$_2$O$_6$ also reveal an anomaly at $\sim 150$ K for the position of the peak at $\sim 597$ cm$^{-1}$ (data not shown). Based on previous studies, the anomaly in resistance at $\sim 110$ K may be related to the change of carrier concentration induced by a structural evolution against temperature.

For La$_3$Ni$_2$O$_6$, an insulating ground state with a checkerboard charge order and AF order based on Ni$^{3+}$ is expected. The average valence of Ni, +1.5, is close to +1.2 that of the superconducting film samples. Evidence for the charge and spin order have been observed. However, superconductivity does not appear up to 25.3
GPAs, where the samples have been metallized. The superconductivity seems to be sensitive to the average-valent state of nickel. In addition, the possible charge and spin order in La$_3$Ni$_2$O$_7$ may suppress superconductivity under pressure. Further synchrotron X-ray and neutron diffraction studies on single crystal samples of the bilayer compounds are necessary to demonstrate the charge and spin order.

In summary, we have grown the bilayer nickelates La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$ single crystals successfully by the floating-zone method with high pressure of oxygen. The structural, magnetic, electronic, and specific heat properties of both compounds are characterized in detail. Electronic measurements show metallic property for La$_3$Ni$_2$O$_7$, and semiconducting for La$_3$Ni$_2$O$_6$ with a thermal activation gap of 55 meV. The resistance, magnetization, and specific heat all reveal a transition-like anomaly at 153 K for La$_3$Ni$_2$O$_7$, suggesting the formation of charge and spin order. In addition, the magnetization of La$_3$Ni$_2$O$_6$ also yields a kink at 176 K, reminiscent to the charge and spin order in La$_3$Ni$_2$O$_7$. Pressure above 6.1 GPa could metallize La$_3$Ni$_2$O$_6$. However, no superconductivity is observed up to 25.3 GPa. Our data suggest the formation of charge and spin order may be a universal characteristic for nickelates with mixed-valent states of nickel.

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