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

Zengjia Liu,$^1$ HuaiLe Sun,$^{1,*}$ Mengwu Huo,$^1$ Xiaoyan Ma,$^{2,3}$ Yi Ji,$^1$ Enkui Yi,$^1$ Lisi Li,$^1$ Hui Liu,$^1$ Jia Yu,$^1$ Ziyou Zhang,$^4$ Zhiqiang Chen,$^4$ Feixiang Liang,$^1$ Hongliang Dong,$^4$ Hanjie Guo,$^5$ Dingyong Zhong,$^1$ Bing Shen,$^1$ Shiliang Li,$^{2,3,5}$ and Meng Wang$^{1,†}$

$^1$Center for Neutron Science and Technology, Guangdong Provincial Key Laboratory of Magnetoelectric Physics and Devices, School of Physics, Sun Yat-Sen University, Guangzhou, 510275, China
$^2$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
$^3$School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, China
$^4$Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China
$^5$Songshan Lake Materials Laboratory, Dongguan, Guangdong, 523808, China

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$_{0.8}$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. Resistance 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$_3$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.

PACS numbers:

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$^{1+}$ (3$d^8$) and Ni$^{2+}$ 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$^{2+}$ ($S = 0$) to a nickelate antiferromagnetic (AF) insulator with Ni$^{3+}$ ($S = 1/2$) 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$_{3n+2}$ by hole doping on the Ln site, such as Sr doped Ln$_{n+1}$Ni$_n$O$_{3n+2}$, 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 +1.29,10. 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.

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$_{3n+2}$, $Ln = $La, Pr, Nd, Sm, and Eu.

| $n$ | Ln$_{n+1}$Ni$_n$O$_{3n+1}$ composition Ni valence | Ln$_{n+1}$Ni$_n$O$_{3n+2}$ composition Ni valence |
|-----|--------------------------------------------------|--------------------------------------------------|
| $∞$ | 113 +3                                            | 112 +1                                            |
| 3   | 4310 +2.67                                         | 438 +1.33                                         |
| 2   | 327 +2.5                                           | 326 +1.5                                          |
| 1   | 214 +2                                             | -                                                 |
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 $n = 1$ La$_2$-Sr$_2$NiO$_4$ and cuprates. A charge density wave (CDW) coincident with the SDW was found in La$_3$Ni$_2$O$_{10}$ and was suggested to result in a metal-to-metal transition. For the topochemically reduced product La$_4$Ni$_3$O$_8$, synchrotron X-ray and neutron diffraction also reveal stacked charge and spin stripe weakly correlated along the c axis. In this case, La$_4$Ni$_3$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 La$_3$Ni$_2$O$_7$ and chemical reduced product La$_3$Ni$_2$O$_6$ consisting of the bilayer NiO$_2$ planes are analogous to the trilayer La$_4$Ni$_3$O$_{10}$ and La$_4$Ni$_3$Os in structural and physical properties. Theoretical calculations for La$_3$Ni$_2$O$_7$ and La$_4$Ni$_3$O$_{10}$ suggest existence of a hidden one-dimensional Fermi surface nesting which would result in CDW instability. For La$_3$Ni$_2$O$_6$ and La$_4$Ni$_3$Os, charge-ordered related structural distortion and magnetic order will emerge in the ground state. The electronic density of states of La$_3$Ni$_2$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 La$_3$Ni$_2$O$_7$ that were synthesized through the soft chemistry method did not reveal evidence of charge or spin order. La$_3$Ni$_2$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 La$_3$Ni$_2$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 La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$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 La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$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 La$_3$Ni$_2$O$_7$ single crystals by a high oxygen pressure floating zone technique and the achievement of La$_3$Ni$_2$O$_6$ single crystals through a subsequent low temperature topochemical reduction method. Electrical resistivity measurements on the single crystals of La$_3$Ni$_2$O$_7$ and La$_3$Ni$_2$O$_6$ show significantly different properties. La$_3$Ni$_2$O$_7$ is metallic while La$_3$Ni$_2$O$_6$ is insulating. Superconductivity has not been realized in La$_3$Ni$_2$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 La$_2$O$_3$ and an excess of 0.5% 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. La$_3$Ni$_2$O$_7$ single crystals were grown with an oxygen pressure at p(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. La$_3$Ni$_2$O$_6$ was obtained from the La$_3$Ni$_2$O$_7$ single crystals by the topochemical reduction method. La$_3$Ni$_2$O$_7$ single crystals were enclosed in an aluminum foil and sealed in vacuum with stoichiometric 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 K$_\alpha$ 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. La₃Ni₂O₇

Crystal structures of La₃Ni₂O₇ and La₃Ni₂O₆ are shown in Fig. 1(a). La₃Ni₂O₇ crystallizes in orthorhombic symmetry (space group: Cmcm) with distorted vertex-sharing NiO₆ octahedra in the close-packed Ni layers. The structure can be termed as inter-growth of two NiO₆ octahedra planes and a La-O fluorite-type layer, stacking along the c direction. La₃Ni₂O₆ with the apical oxygen atoms removed crystallizes in tetragonal symmetry (space group: I4/mmm). The structure is stacked by two corner-sharing square NiO₆ planes and a La-O fluorite-type layer along the c direction.

The insets in (b) and (c) are diffraction patterns in reciprocal space on corresponding single crystals collected on a single crystal X-ray diffractometer.

FIG. 1: (a) Sketches of the crystal structures of La₃Ni₂O₇ and La₃Ni₂O₆. A photo of the single crystal of La₃Ni₂O₇. (b) X-ray diffraction patterns integrated from single crystal diffraction on La₃Ni₂O₇ and (c) La₃Ni₂O₆. The insets in (b) and (c) are diffraction patterns in reciprocal space on corresponding single crystals collected on a single crystal X-ray diffractometer.

The valent states of Ni are crucial for realization of charge and spin order. La₃Ni₂O₇ is metallic, where nickel ions could host a valence of +2.5, or a mixed-valent states of +2 and +3. Figure 2(a) shows the XPS spectrum of Ni ions in La₃Ni₂O₇. As a comparison, an XPS spectrum of Ni²⁺ measured on NiO is presented in Fig. 2(b). The main peaks of the spectrum of Ni²⁺ 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 La₃Ni₂O₇ 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 Ni²⁺ as measured on NiO and fit the spectrum of La₃Ni₂O₇. A peak at 855.7 eV could be separated, yielding the existence of the trivalent oxidation state of Ni³⁺. Thus, our XPS measurements reveal that the valent states of nickel in La₃Ni₂O₇ are a mixture of the divalent Ni²⁺ and trivalent Ni³⁺ oxidation states.

Figure 3(a) shows the temperature dependence of the resistance for La₃Ni₂O₇ single crystals, revealing a metallic ground state that is analogous to the n = 3, and ∞ RP compounds. We observe two anomalies in resistance, one at ~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.
TABLE II: Structural parameters for single crystals of La$_3$Ni$_2$O$_7$ and La$_4$Ni$_3$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$_4$Ni$_3$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 |
|                   | $c = 20.455(4)$ Å | $c = 19.368(4)$ Å |
| $\alpha = \beta = \gamma = 90^\circ$ | $\alpha = \beta = \gamma = 90^\circ$ |

|                    | La1   | La2   | Ni | O1 | O2 | O3 | O4 |
|--------------------|-------|-------|----|----|----|----|----|
|                     | (0.32, 0.75, 0.25) | (0.5, 0.25, 0.75) | (0.40, 0.75, 0.75) | (0.41, 1, 1) | (0.5, 0.71, 0.75) | (0.40, 0.5, 0.5) | (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 110 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 redlines 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, $C_{ph} = 9R \sum_{n=1}^{2} C_n \left( \frac{T}{\theta_{Dn}} \right)^3 \int_0^{\theta_{Dn}/T} x^4 e^x \left( e^x - 1 \right)^2 dx$, 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$_4$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$^{15,16}$. 
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. \(\text{La}_3\text{Ni}_2\text{O}_6\)

The ground state of \(\text{La}_3\text{Ni}_2\text{O}_6\) with mixed Ni$^{2+}$d$^9$($S = 1/2$) and Ni$^{2+}$d$^0$($S = 0$) 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.\(^{28}\) However, only was the insulating state confirmed due to the limitation of powder samples. We obtain single crystals of \(\text{La}_3\text{Ni}_2\text{O}_6\) from topochemical reduction of the \(\text{La}_3\text{Ni}_2\text{O}_7\) 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.\(^{29}\) The resistivity of \(\text{La}_3\text{Ni}_2\text{O}_6\) displays a weak kink at 101 K. In contrast to the abrupt change in resistivity at $\sim$100 K for \(\text{La}_4\text{Ni}_3\text{O}_{10}\) that corresponds to the formation of charge and spin stripe order.\(^{18,19}\)

By fitting the resistivity to the activation-energy model $\rho(T) = \rho_0 \exp(E_a/k_B T)$, 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 \(\text{La}_3\text{Ni}_2\text{O}_6\), 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 \(\text{La}_3\text{Ni}_2\text{O}_6\) 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 \(\text{La}_3\text{Ni}_2\text{O}_6\), 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.\(^{13}\) 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 \(\text{La-Ni-O}\) system tend to form charge and spin order. The emergence of the two types of order has been verified in hole doped \(\text{La}_2-x\text{Sr}_x\text{NiO}_4\) ($x = 1/4$, 1/3, and 1/2), \(\text{La}_4\text{Ni}_3\text{O}_{10}\), and \(\text{La}_4\text{Ni}_3\text{O}_8\).\(^{18,19,44-46}\) 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 \(\text{La}_3\text{Ni}_2\text{O}_6\) single crystals compared to that of \(\text{La}_4\text{Ni}_3\text{O}_{10}\). The possibility that the charge order emerges in the bilayer \(\text{La-Ni-O}\) 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 \(\text{La}_3\text{Ni}_2\text{O}_7\) 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.\(^{20-24}\)

For \(\text{La}_3\text{Ni}_2\text{O}_6\), an insulating ground state with a checkerboard charge order and AF order based on Ni$^{1+}$ is expected.\(^{28}\) 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.

V. ACKNOWLEDGMENTS

Work was supported by the National Natural Science Foundation of China (Grants No. 12174454, 11904414, U2130101), the Guangdong Basic and Applied Basic Research Foundation (No. 2021B1515120015), and National Key Research and Development Program of China (No. 2019YFA0705702, 2020YFA0406003, and 2021YFA1400401, 2021YFA0718900).
31 J. Zhang, H. Zheng, Y.-S. Chen, Y. Ren, M. Yonemura, A. Huq, and J. Mitchell, Physical Review Materials 4, 083402 (2020).
32 W. Cai, H. Sun, W. Xia, C. Wu, Y. Liu, H. Liu, Y. Gong, D.-X. Yao, Y. Guo, and M. Wang, Physical Review B 102, 144525 (2020).
33 H. Sun, C. Chen, Y. Hou, W. Wang, Y. Gong, and M. Huo, Science China: Physics, Mechanics and Astronomy 64, 118211 (2021).
34 H. M. Rietveld, J. Appl. Cryst. 2, 65 (1969).
35 V. V. Poltavets, K. A. Lokshin, S. Dikmen, M. Croft, T. Egami, and M. Greenblatt, Journal of the American Chemical Society 128, 9050 (2006).
36 L. Qiao and X. Bi, Epl 93, 57002 (2011).
37 Y. Liu, P. Liu, W. Qin, X. Wu, and G. Yang, Electrochimica Acta 297, 623 (2019).
38 H. Chen, Z. Wu, Y. Zhong, T. Chen, X. Liu, J. Qu, W. Xiang, J. Li, X. Chen, X. Guo, et al., Electrochimica Acta 308, 64 (2019).
39 F. Rivadulla, J.-S. Zhou, and J. Goodenough, Physical Review B 67, 165110 (2003).
40 C. Liu, V. F. Humbert, T. M. Bretz-Sullivan, G. Wang, D. Hong, F. Wrobel, J. Zhang, J. D. Hoffman, J. E. Pearson, J. S. Jiang, et al., Nature Communications 11, 1402 (2020).
41 L. Li, N. Narayanan, S. Jin, J. Yu, Z. Liu, H. Sun, C.-W. Wang, V. K. Peterson, Y. Liu, S. Danilkin, et al., Physical Review B 102, 094413 (2020).
42 L. Ortega-San Martin, J. P. Chapman, L. Lezama, J. Sánchez Marcos, J. Rodríguez-Fernández, M. I. Arriortua, and T. Rojo, European Journal of Inorganic Chemistry 2006, 1362 (2006).
43 K. Rajeev, G. Shivashankar, and A. Raychaudhuri, Solid State Communications 79, 591 (1991).
44 C. H. Chen, S.-W. Cheng, and A. S. Cooper, Physical Review Letters 71, 2461 (1993).
45 S. H. Lee and S.-W. Cheong, Physical Review Letters 79, 2514 (1997).
46 R. Zhong, B. L. Winn, G. Gu, D. Reznik, and J. M. Tranquada, Physical Review Letters 118, 177601 (2017).