Pressure studies on the electrical properties in $R_{2-x}Sr_xNi_{1-y}Cu_yO_{4+\delta}$ $(R=La, Nd)$ and $La_3Ni_2O_{7+\delta}$

T. Hosoya, K. Igawa, Y. Takeuchi, K. Yoshida, T. Uryu, H. Hirabayashi and H. Takahashi

College of Humanities & Sciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-Ku, Tokyo, 156-8550, Japan

origuti_hm1@hotmail.co.jp

Abstract. The Ruddlesden-Popper series of compounds $La_{n+1}Ni_nO_{3n+1}$ are one of the strongly correlated electron systems. Among these compounds, $La_3NiO_4$ ($n=1$) is a well-known two-dimensional antiferromagnetic insulator. Electrical resistivity under high pressure have been measured on $R_{2-x}Sr_xNi_{1-y}Cu_yO_{4+\delta}$ ($R=La, Nd$) up to 2 GPa and $La_3Ni_2O_{7+\delta}$ up to ~20 GPa. Electrical resistivity of $La_{1.92}Sr_{1.08}NiO_4$ under high pressure reveals an enhancement of the electronic localization under pressure. On the other hand, in case of $Nd_{1.6}Sr_{0.4}Ni_{0.6}Cu_{0.4}O_{4+\delta}$, a metal-insulator transition is observed at ~240 K and a metallic state is favorable under pressure, in contrast to $La_{1.92}Sr_{1.08}NiO_4$. In $La_3Ni_2O_{7+\delta}$ pressure also enhances a metallic state up to 2 GPa.

1. Introduction

Since the discovery of high-$T_C$ superconductors, a lot of investigations have been performed for transition-metal oxides. Although many kinds of superconductors have been discovered, a mechanism of the high temperature superconductivity is still controversial. The $La_{2-x}Sr_xCuO_4$ (LSCO) with a $K_2NiF_4$-type structure has been studied extensively, because it is a prototypical high-$T_C$ superconducting compound with $T_C = 39$ K at $x = 0.15$ [1]. Non-doped compound $La_2CuO_4$ is a two-dimensional antiferromagnetic insulator with $S=1/2$, and has a charge-transfer gap $\Delta = \sim 2$ eV [2]. Hole-doping by substitution of $Sr^{2+}$ for $La^{3+}$ suppresses the antiferromagnetic order and causes a metal-insulator transition at $x \sim 0.05$. These high-$T_C$ oxides are related to the fundamental problem of the metal-insulator transitions in strongly correlated electron systems. An analogous $La_{2-x}Sr_xNiO_4$ (LSNO) with a similar $K_2NiF_4$-type structure has been also investigated extensively. $La_2NiO_4$ is an antiferromagnetic insulator with $S=1$, which shows charge and spin stripe ordering in NiO$_2$ plane[3] and becomes metallic with doping of $Sr^{2+}$ for $La^{3+}$. The charge and/or spin stripe ordering has been also found in the high-$T_C$ superconductors, $La_{2-x}Ba_xCuO_4$ and $La_{2-x-y}Nd_xSr_yCuO_4$, having the similar crystal structure [4]. In LSNO much more hole-doping ($x>1$) is needed to cause the insulator-metal transition [5], because the LSNO has the large charge-transfer gap of 3.5~4 eV that depends on the strength of the metal-oxygen hybridization, and a strong electron-phonon interaction which could relate to the formation of small polarons [6]. The ternary $La$-$Ni$-$O$ compounds are included in the Ruddlesden-Popper series of compounds $La_{n+1}Ni_nO_{3n+1}$. $La_2NiO_4$ ($n=1$) is the starting compound of LSNO and $La_3Ni_2O_{7+\delta}$ ($n=2$) possesses two perovskite-type Ni-O layers separated by single rocksalt LaO layers along $c$-direction [7]. $La_3Ni_2O_7$ has rather low electrical resistivity and shows metallic behavior at room temperature because of an enhancement of Ni-O-Ni overlapping along $c$-direction. However, the electrical resistivity of $La_3Ni_2O_{7+\delta}$ shows the phase transition at $T_C=140$K, which is
considered to be related to the charge ordering, and insulating below \(T_C\). The \(T_C\) has been reported to decrease with increasing pressure up to 1.5 GPa [8] and \(\sim 12\) GPa is estimated to destroy \(T_C\), if it decreases with increasing pressure with the same rate as below 1.5 GPa. In the hole-doped \(La_2NiO_4\) \((n=1)\) system, there has been a few high pressure experiments only using the piston-cylinder device [9,10], while a lot of high pressure research for cuprate has revealed the several interesting features in high-\(T_C\) superconductors[11]. The high pressure experiments are expected to play an important role for the investigation of the metal-insulator transition and the metallic state of nickelates, because in general the pressure decreases the charge-transfer gap in the nickelates and enhances the metallic phase through increase of the metal-oxygen hybridization.

In this paper, we report the pressure dependence of electrical resistivity of polycrystalline \(La_{2-x}Sr_xNiO_4\), \(R_{2-x}Sr_xNi_{1-y}Cu_yO_4+\delta\) \((R=\text{La, Nd})\) and \(La_3Ni_2O_7+\delta\), which show the metal-insulator transition. A piston-cylinder apparatus and a diamond anvil cell (DAC) were used for high pressure experiments up to 2.5 GPa and 20 GPa, respectively. The \(Nd_{2-x}Sr_xNi_{1.7}Cu_0.3O_4+\delta\) with a similar crystal structure to LSNO are studied to reveal the crossover properties between nickel oxides and cupper oxides.

2. Experimental

The \(La_{2-x}Sr_xNiO_4\) \((0 \leq x \leq 1.08)\) samples were prepared by sintering method using high-purity \(La_2O_3\), \(SrCO_3\) and \(NiO\) in stoichiometric quantities [5]. The \(Nd_{2-x}Sr_xNi_{1.7}Cu_0.3O_4\) \((0 \leq x \leq 1)\) samples were prepared by co-precipitation method using high-purity \(Nd_2O_3\), \(SrCO_3\), \(NiO\) and \(CuO\) in stoichiometric quantities [12]. The \(La_3Ni_2O_7+\delta\) samples were prepared by co-precipitation using high-purity \(La_2O_3\) and \(NiO\) in stoichiometric quantities [8]. Powder X-ray diffraction(XRD) data, collected on a RINT2500 diffractometer with monochromatized CuKα radiation, were used to monitor the completion of the reaction. Least-squares refinement of the observed powder diffraction data \((10^\circ \leq 2\theta \leq 90^\circ)\) was used in the evaluation of cell parameters. The electrical resistivity measurements under high pressure were carried out by a DC four-probe method using piston-cylinder device up to 2.0 GPa, with Fluorinert(FC-77:FC-70=1:1) as the pressure transmitting medium. Diamond anvil cell(DAC) was used for the measurement under high pressure up to 20 GPa, using NaCl as the pressure transmitting medium and Al_2O_3 powder for electrical insulation.

3. Results and Discussion

3.1. \(La_{2-x}Sr_xNiO_4\) (LSNO)

Wu and Neumeier [10] reported the pressure dependence of the electrical resistivity up to 1.6 GPa in highly doped \(La_{0.9}Sr_{1.1}NiO_4\) which shows the metal-insulator transition at \(T_{M-I} = 238\) K. They also reported the \(T_{M-I}\) decreases with applying pressure drastically at a rate of \(-55.8\) K/GPa, but pressure higher than \(\sim 1\) GPa slightly increases \(T_{M-I}\). They estimated the pressure effect on the charge-transfer gap from the results of pressure dependence of \(T_{M-I}\) based on the model of variable range hopping of a small polaron. From the results that pressure weakly affects the resistivity at a rate of \(-6.9\)%/GPa and \(T_{M-I}\) cannot be completely suppressed, they suggested that the applied pressure does not appreciably change the localized states at Fermi level. We have measured the electrical resistivity of \(La_{0.92}Sr_{1.08}NiO_4\) having \(T_{M-I} = 80\) K under high pressure up to 2 GPa. The \(T_{M-I}\) shows to increase with pressure up to 2 GPa at a rate of \(+10\) K/GPa, which is opposite to the previous data [10]. However, this is similar behavior when it is compared with the previous data above \(\sim 1\) GPa. Our results simply suggest that the charge-transfer gap increases with increasing pressure. However, it should be considered that the electronic localization is enhanced by the electron-phonon interaction and the small polaron formation with increasing pressure as studied in \(La_{2-x}Sr_xMnO_3\) [13].

We also carried out the pressure dependence of electrical resistivity in \(La_{1.7}Sr_{0.3}NiO_4\) which shows the sudden change in the resistivity at \(T_{CO} = 241\) K, attributed to the charge ordering phenomenon. The \(T_{CO}\) decreases with pressure up to 2.5 GPa at a rate of \(-1.1\) K/GPa, which is consistent with the previously reported data measured up to 1.3 GPa [9], though the change rate of \(-1.1\) K/GPa is rather
high. This behavior is similar to the case of \( \text{La}_{2-x}\text{Ba}_x\text{Cu}_4\text{O}_8 \) with \( x=1/8 \) in LTT phase, in which the charge ordering (charge stripe) is suppressed by pressure [14].

3.2. \( \text{Nd}_{2-x}\text{Sr}_x\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta} \)

The \( \text{Nd}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta} \) have also been investigated like as the LSNO. The metal-insulator transition was reported to occur in samples with high Sr concentration \( x \geq 0.9 \) [12,15] as observed in LSNO. In the \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta} \) the substitution of La with smaller isovalent Nd causes an increase of the chemical pressure on the NiO\( _2 \) plane. Since this chemical pressure enhances orthorhombic distortion due to the mismatch between NiO\( _2 \) and NdO layer, \( \text{Nd}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta} \) shows orthorhombic to tetragonal structural transition at \( x = 0.45 \) which is higher concentration than \( x = 0.22 \) of LSNO [16]. The value of \( T_{\text{CO}} \) prominently observed at \( x = 1/3 \) in \( \text{Nd}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta} \) is similar one reported in LSNO. These charge ordering phenomena are reported to be related to the orthorhombic distortion in both cuprates and nickelates [16]. Thus it is possible to compare the pressure effect on the charge ordering in the orthorhombic and tetragonal phase, and these will be investigated in near future. In this study the substitution of Cu for Ni is carried out in order to obtain more conductive state. In Fig. 1 we show the electrical resistivity of \( \text{Nd}_{1.6}\text{Sr}_{0.4}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta} \) as a function of temperature. With increasing Cu concentration the electrical resistivity decreases and a metal-insulator transition is observed at \( \sim 240 \) K at \( y = 0.5 \). However, the metal-insulator transition was not observed except for \( y = 0.5 \). On the other hand, Chaker et al. reported that the substitution of Cu for Ni in \( \text{NdSrNiO}_4 \) enhances the electrical resistivity, which is opposite to our data [17]. They explained that the transfer of electron from \( d_{x^2-y^2} \) to \( d_z^2 \) by introduction of Cu causes the increase of the electrical resistivity. On the other hand, since the average valence of Ni in \( \text{Nd}_{1.6}\text{Sr}_{0.4}\text{NiO}_4 \) is 2.4, the substituted Cu does not decrease conductive \( d_{x^2-y^2} \) electrons in our case. Moreover since cuprate has smaller charge-transfer gap, the substitution of Cu for Ni might decrease it. In Fig. 2 we show the electrical resistivity of \( \text{Nd}_{1.6}\text{Sr}_{0.4}\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4+\delta} \) for each pressure. The metal-insulator transition is observed at \( T_{\text{M-I}} \sim 240 \) K at 0.5 GPa and \( T_{\text{M-I}} \) decreases with applying pressure. However, the \( T_{\text{M-I}} \) decreases down to \( \sim 220 \) K under pressure of 1.0 GPa and remains constant above 1 GPa.

![Figure 1](image1.png)

**Figure 1.** Electrical resistivity of \( \text{Nd}_{1.6}\text{Sr}_{0.4}\text{Ni}_{1-y}\text{Cu}_y\text{O}_{4+\delta} \) as a function of temperature. A metal-insulator transition is seen in \( x=0.5 \).

![Figure 2](image2.png)

**Figure 2.** Electrical resistivity of \( \text{Nd}_{1.6}\text{Sr}_{0.4}\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4+\delta} \) for each pressure. The electrical resistivity decreases with pressure and the metal-insulator transition temperature \( T_{\text{M-I}} \) indicated by arrows is suppressed by increase of pressure.
3.3. $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$

The $T_c$ is observed at 137 K as a sudden change of electrical resistivity in $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$. This phase transition is considered to be related to the charge ordering. The value of $T_c$ is similar to the previously reported one [7,8]. In Fig 3 we show the normalized electrical resistivity of $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ for each pressure using the piston-cylinder device. It is seen in Fig 3 that the $T_c$ decreases with increasing pressure at a rate of -12.5 K/GPa, which is close to the reported value of -10.7 K/GPa [8], and the sudden change becomes sluggish at higher pressure. From the results of decrease of the electrical resistivity under pressure, pressure is thought to enhance the Ni-O-Ni overlap along $c$-direction, although we do not have any structural data under high pressure yet. If the $T_c$ decreases linearly with pressure at the observed rate, pressure would destroy the charge ordered state at ~10GPa. In Fig 4 we show the electrical resistivity of $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ for each pressure using a DAC up to ~20 GPa. No metallic behavior over all temperature range are shown and the $T_c$ hardly seen in Fig 4. The reason why no metallic state was observed is that extra stresses on the sample and/or a grain boundary effect might be emerged, since liquid was not used as pressure transmitting medium.

![Figure 3](image1.png)

**Figure 3.** Normalized electrical resistivity of $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ for each pressure. It is normalized at the value at room temperature. $T_c$ decreases with increasing pressure at a rate of -12.5 K/GPa.

![Figure 4](image2.png)

**Figure 4.** Electrical resistivity of $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ for each pressure using a DAC. No metallic behavior is observed and $T_c$ is hardly observed.

4. Conclusion

We have studied the pressure effect on electrical resistivity of $\text{La}_{1.92}\text{Sr}_{1.08}\text{NiO}_4$, $\text{Nd}_{1.6}\text{Sr}_{0.4}\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4+\delta}$ and $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$. It is observed in $\text{La}_{1.92}\text{Sr}_{1.08}\text{NiO}_4$, $T_{M-I}$ increases with pressure up to 2 GPa. In these results it is found that the pressure effect does not correspond to the hole-doping effect, which is often observed high-$T_c$ superconductors [11]. On the other hand, in $\text{Nd}_{1.6}\text{Sr}_{0.4}\text{Ni}_{0.5}\text{Cu}_{0.5}\text{O}_{4+\delta}$, $T_{M-I}$ decreases with pressure up to 2 GPa. It is inferred that the copper-oxygen bonding might be strengthened by pressure much more than the case of nickelates. Though the results of pressure dependence of $T_c$ in $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ up to 2.0 GPa indicates the consistency with previously reported data. The results using the DAC shows the enhancement of the insulating phase. The structural data under high pressure are definitely needed for detail consideration.
References
[1] Takagi H, Ido T, Ishibashi S, Uota M, Uchida S and Tokura Y, 1989 Phys. Rev. B40 2254.
[2] Uchida S, Ido T, Takagi H, Arima T, Tokura Y and Tajima S, 1991 Phys. Rev. B43 7942.
[3] R.Kajimoto, K.Ishizaka, H.Yoshizawa, Y.Tokura, 2003 Phys. Rev. B67 014511, S.Cheong, H.Hwang, C.Chen, B.Batlogg, L.Rupp, S.Carter, 1994 Phys.Rev. B49 7988
[4] Tranquada J M, Sternlieb B J, Axe J D, Nakamura Y and Uchida S, 1995 Nature 375 561.
[5] R.J.Cava, B.Batlogg, T.T.Krajewski, W.F.Peck,Jr, A.P.Ramirez, L.W.Rupp.Jr, 1991 Phys. Rev. B43 1229, S.Shinomori, Y.Okimoto, M.Kawasaki, Y.Tokura, 2002 J. Phys . Soc. Jpn 71 705.
[6] T.Ido, K.Magishi, H.eisaki, S.Uchida, 1991 Phys. Rev. B44 12094.
[7] Fukamachi.T, Oda.K, Kobayashi.Y, Miyashita.T, Sato.M, J. Phys . Soc. Jpn 70 2757.
[8] Wu G, J.J.Neumeier, M.F.Hundle, 2001 Phys. Rev. B63 245120
[9] S.H.Han, M.B.Maple, Z.Fisk, S-W.Cheong, A.S. Cooper, O.Chmaissem, J.D.Sullivan, M.Mareazio 1995 Phys. Rev. B52 1347.
[10] Wu G and J.J.Neumeier, 2003 Phys. Rev. B67 125116.
[11] Takahashi H and Mori N, 1996 Studies of High Temperature Superconductors 16 1-63.
[12] Arbuckle B W, Ramanujachary K V, Zhang and Greemblatt M, 1990 J.Solid State Chemistry 88 278.
[13] Zhou J -S, Goodenough J B, Asamitsu A and Tokura Y, 1997 Phys. Rev. Lett. 79 3234.
[14] Mori N, Takai M, Tomioka A, Ogawa S, Ueda Y, Takahashi H and Katano S, 1994 J. of Supercond. 7 462.
[15] Takeda,Y, Nishijima.M, Imanishi.N, Kanno,R, Yamamoto,O, Takano,M, 1992 J.Solid State Chemistry 96 72, Doyle S M, Sridhar Kumar M P and McK Paul D, 1992 J. Phys.: Condens. Matter 4 3559.
[16] Hucker M, Zimmermann M, Klingler R, Kiele S, Geck J, Bakehe S N, Zhang J Z, Hill J P, Revolevshi A, Buttry D J, Buchner B, Tranquada J M, 2006 Phys. Rev. B74 085112, K.Ishizuka, Y.Taguchi, R.Kajimoto, H.Yoshizawa, Y.Tokura, 2003 Phys. Rev. B67 184418.
[17] Chaker.H, T.Roisnel, O.Cador, R.Ben Hassen, 2004 J. Solid State Chem 4067.