Electrical Resistivity Measurements under High Pressure for $Nd_{3.5}Sm_{0.5}Ni_3O_8$

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$Nd_{3.5}Sm_{0.5}Ni_3O_8$ is a candidate for high-T_c superconductor, due to the close structural and electrical similarities with high-T_c cuprates. In electrical resistivity measurement, $Nd_{3.5}Sm_{0.5}Ni_3O_8$ shows a semiconducting behavior. However, by intercalation and subsequent deintercalation treatments with sulfur, $Nd_{3.5}Sm_{0.5}Ni_3O_8$ displays metallic behavior down to 20 - 40 K, followed by the weak semiconducting tendency at lower temperatures. In this study, the electrical resistivity measurements under high pressures up to 2 GPa were performed for a semiconducting sample of $Nd_{3.5}Sm_{0.5}Ni_3O_8$. We discuss the electrical properties of this material, combining the high-pressure resistivity data with measurements on metallic samples at ambient pressure.

1. Introduction

$Nd_{3.5}Sm_{0.5}Ni_3O_8$ contains 2-dimensional NiO_2 planes and its crystal structure is basically the same with high-T_c cuprates such as $Bi_2Sr_2Ca_2Cu_3O_y$, in which three CuO_2 planes are separated by insulating block layers. Moreover, the formal valence of Ni is +1.33 consisting of Ni^+ $3d^9$ and Ni^{2+} $3d^8$ states. Despite these structural and electrical similarities with cuprates, $Nd_{3.5}Sm_{0.5}Ni_3O_8$ had showed neither metallic characteristic nor superconductivity [1, 2]. However, the close similarities to the cuprates lead us to expect that high-T_c superconductivity may be induced in this material by tuning its electronic state appropriately, for example, by carrier-doping or applying pressure.

Theoretical and experimental studies have been performed for $La_4Ni_3O_8$, which has the same structure as $Nd_{3.5}Sm_{0.5}Ni_3O_8$ [3-13]. Theoretical calculations have predicted the metallic state mainly due to the Ni-$3d_{x2-y2}$ orbital. One theory predicts a metallic state for $T > 105$ K and an insulating state for $T < 105$ K, due to a transition between a low-spin and a high-spin state [10, 11]. However, in electrical resistivity (ρ) measurement, $La_4Ni_3O_8$ exhibits semiconducting behaviour even at high temperatures. Regarding the discrepancy between theory and experiment, no clear answer has been obtained. The ρ of $La_4Ni_3O_8$ at high pressure indicates that the semiconducting behaviour is suppressed, but neither the metallic state nor superconductivity has been observed [13].

Recently, we found that $Nd_{3.5}Sm_{0.5}Ni_3O_8$ shows metallic behavior down to approximately 20 K after intercalation and subsequent deintercalation with sulfur. This is the first observation of the metallic state in this system [14]. In a more recent study, it has been found that the behavior of ρ depends strongly on the condition of deintercalation and that the metallic state emerges from room temperature down to 20-40 K. It is unclear why sulfur intercalation and deintercalation induce metallic state. The block layer separating the NiO_2 planes is of the fluorite type, similar to that of a T'-type high-T_c cuprate. It is known that the T'-type structure tends to incorporate additional oxygen atoms into the apical oxygen site in fluorite-type block layers and that this oxygen is a

strong obstacle to superconductivity [15]. We speculate that additional oxygen also exists in the present system and that sulfur works as a "getter" removing the additional oxygen that impedes metallic conduction. At low temperatures, however, the weak localization of resistivity still remains and this may be one of the obstacles preventing the occurrence of superconductivity. In this study, the semiconducting $Nd_{3.5}Sm_{0.5}Ni_3O_8$ sample *without* sulfur treatment was used for the electrical resistivity measurements at pressures up to 2 GPa to determine whether or not the semiconducting nature of the material could be suppressed. In a previous paper, we have already reported the ρ data at pressures up to 3 GPa [2]. However the quality of previous sample was not as good as that used in the present work. The sample quality was greatly improved by optimizing the synthesis procedure (for example, ρ is ~1 Ω cm for the present sample at 300 K, and it was ~10^2 Ω cm in the previous sample). In this paper, we can thus provide more reliable data than in our previous report.

2.   Experimental

At first $Nd_{3.5}Sm_{0.5}Ni_3O_{10}$ was synthesized by solid-state reaction, and the detail was reported in our previous paper [1]. Next, $Nd_{3.5}Sm_{0.5}Ni_3O_{10}$ was annealed for 5 h at 350 °C under flowing hydrogen to reduce $Nd_{3.5}Sm_{0.5}Ni_3O_{10}$ to $Nd_{3.5}Sm_{0.5}Ni_3O_8$. This reduction process produces $Nd_{3.5}Sm_{0.5}Ni_3O_8$ in powder form. The powder sample was then pressed at 3 GPa into a pellet with dimensions of ϕ 5 mm $\times$ 1 mm using a cubic-anvil-type apparatus at room temperature. Resultant high pressed $Nd_{3.5}Sm_{0.5}Ni_3O_8$ pellet was next annealed at 350 °C for 3 h to remove the internal strains caused by the high-pressure press. We refer to this sample hereafter as the "as-synthesized sample".

Sulfur-intercalation was performed by using a high-pressed $Nd_{3.5}Sm_{0.5}Ni_3O_8$ pellet in an evacuated Pyrex® glass tube (ϕ 4.6 mm $\times$ 140 mm) together with an another sulfur pellet at 300 °C for 60 h. The weight of sulfur pellet was 6 wt. % comparing to that of $Nd_{3.5}Sm_{0.5}Ni_3O_8$. The size of both the pellet and the glass tube is important for obtaining metallic property. Sulfur-deintercalation was performed in tube furnace at 280 or 290 °C for 15-25 h under flowing hydrogen gas. We call these samples the "S-deintercalated samples" hereafter.

The samples were checked by X-ray diffraction (XRD) using Cu Kα radiation. The electrical resistivity measurements were performed using a conventional four-probe method. For the high-pressure experiments, a hybrid pressure cell (Be-Cu and NiCrAl) was used with Glycerin as the pressure medium.

3.   Results and discussion

Fig. 1 shows the XRD pattern for the as-synthesized and S-deintercalated samples of $Nd_{3.5}Sm_{0.5}Ni_3O_8$. The XRD patterns indicate that the samples are single phases. The lattice constants for each sample can be calculated by tetragonal cell with approximately a = 3.91 Å and c = 25.28 Å. It can be noticed that in the S-deintercalated samples, the S/N ratio seems to be worse than that in the as-synthesized sample. It is suggested that the perfection of crystal is degraded by the intercalation and subsequent deintercalation processes. In a previous work, we reported that the c-axis length shrank by the sulfur-deintercalation, possibly due to the removal of the additional apical oxygen [14]. However, in the present work, clear shrinkage of the c-axis length by deintercalation was not observed. The c-axis length seems to be almost unchanged regardless of deintercalation condition. The quality of the samples used in this work is better (the S/N is better in the X-ray data) than that of previous samples by the improvement of synthesis condition. Therefore, the result of lattice constant reported here is more reliable than our previous result. For this reason, it is premature to conclude that the c-axis shrinks by sulfur-deintercalation. More detailed crystal structure analyse using synchrotron or neutron diffraction are needed to settle this issue.

Fig. 2 shows the temperature dependence of the electrical resistivity for the as-synthesized sample. At ambient pressure, ρ increases as the temperature decreases. The semiconducting behaviour weakens at approximately 170 K, showing the plateau-like feature ranging from approximately 170 to 100 K in the resistivity curve. Similar plateau-like behaviour has also been observed in $La_4Ni_3O_8$ from approximately 180 to 100 K [13]. This has been interpreted to mean that 180 K is the onset temperature for critical antiferromagnetic fluctuations in $La_4Ni_3O_8$, considering the NMR result [8].

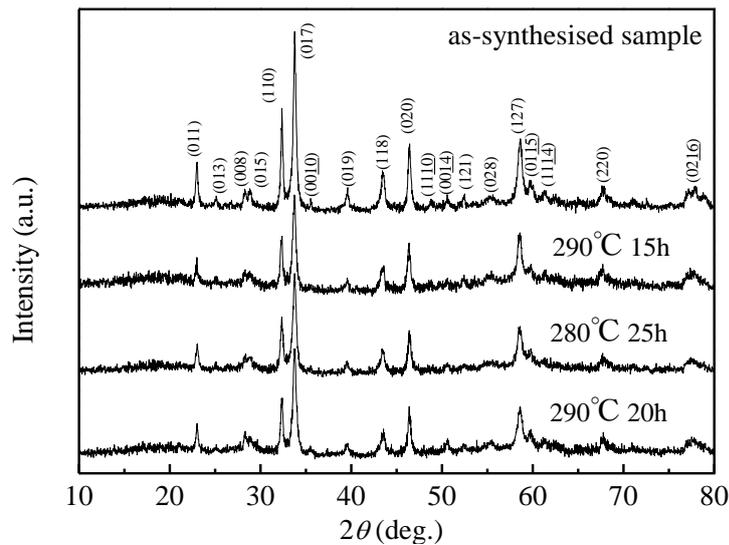**Fig. 1.** XRD patterns of as-synthesized and S-deintercalated samples of $Nd_{3.5}Sm_{0.5}Ni_3O_8$. For the S-deintercalated samples, the deintercalation temperature and time are displayed in the figure.

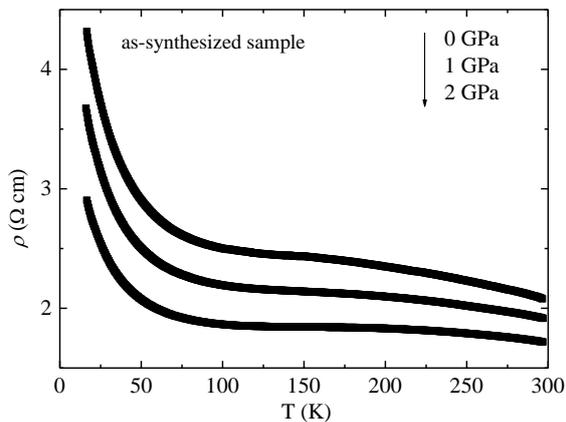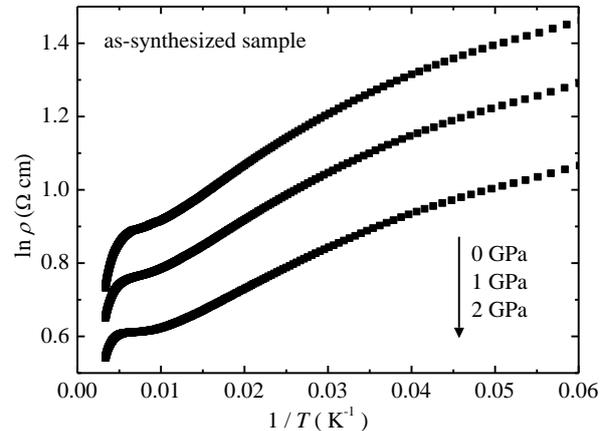**Fig. 2.** Temperature dependence of ρ for the as-synthesized sample of $Nd_{3.5}Sm_{0.5}Ni_3O_8$ under pressure.

Fig. 3. The Arrhenius-plot for the as-synthesized sample of $Nd_{3.5}Sm_{0.5}Ni_3O_8$ under pressure.

A sharp jump in ρ observed in $La_4Ni_3O_8$ at 105 K is absent in our sample. It has recently been revealed that the origin of this feature is due to charge order [16].

In our sample, the charge order might be melted by chemical pressure. As the pressure increases, the value of ρ decreases at all measured temperature range. In order to look into more detailed change of ρ by pressure, the Arrhenius-plot is presented in Fig. 3.

As can be noticed in this figure, the anomaly around 170 K ($1/T \sim 0.006$) can be clearly seen. The activation energy at $T > \sim$170 K seems to be suppressed by pressure but at $T < \sim$170 K, the

activation energy little changes by pressure. As discussed below, the semiconducting behaviour at low temperatures may come mainly from the randomness in the crystal, so that the gains of the kinetic energy of the carriers by pressure of up to 2 GPa cannot overcome the random potentials. It can be seen that the $d\rho / dT$ at approximately 100 to 170 K is very small. Especially in the 2 GPa data, $d\rho /dT$ is almost zero in this temperature range. This suggests that metallization by pressure would start at 170 K. If this is true, antiferromagnetic fluctuations play a very important role for the metallic transport properties of this system. In order to clarify this issue, higher-pressure experiments are needed.

In Fig. 4, the temperature dependence of ρ for the samples treated with various sulfur-deintercalation conditions are plotted together with data for the as-synthesized sample under pressure. The ρ of the S-deintercalated samples are multiplied by factors of 8 and 20 in order for easy comparison with data for the as-synthesized sample. In the 290 °C 15 h S-deintercalated sample, ρ weakly increases from room temperature as cooling and starts to decreases at approximately 170 K, showing metallic behaviour down to approximately 70 K. This behaviour somewhat resembles the data of the as-synthesized sample at 2 GPa, indicating that the 170-K-anomaly observed in the as-synthesized sample might be the precursor of metallization. The other two S-deintercalated samples show metallic behaviour down to $T > \sim35$ K. However at lower temperatures, ρ shows a weak semiconducting upturn, as shown in Fig. 5. It can be noticed in Fig. 4 that the system enters into a metallic state when ρ decreases down to be 10^{-2} Ω cm-order at room temperature. Even assuming that ρ of a polycrystal sample is an order of magnitude larger than that of a single crystal based on experimental results for this type of oxide, this ρ value (10^{-2} Ω cm) is very large for a metallic state and suggestively exceeds the Mott-Ioffe limit, indicating the anomalous transport mechanism. This is similar to experimental results for high-quality polycrystal samples of $La_{2-x}Sr_xCuO_4$, in which the insulator-metal transition occurs when the room-temperature value of ρ is approximately 10^{-2} Ω cm with Sr content x between 0.006 and 0.01 [17], suggesting the similarity of transport mechanism between the present system and high-T_c cuprate. In metallic samples, ρ shows a broad slope change from approximately 200 to 100 K, implying that this is related to the 170-K-anomaly seen in the as-synthesized sample. This can be clarified by experiments at higher pressures than 2 GPa for the as-synthesized sample.
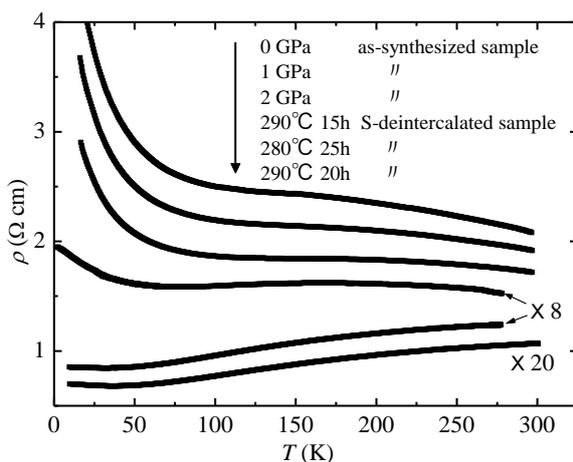

Fig. 4. Temperature dependence of ρ of the as-synthesized sample under pressure and of S-deintercalated samples of $Nd_{3.5}Sm_{0.5}Ni_3O_8$. The ρ of three S-deintercalated samples are multiplied by factors of 8 and 20 for easy comparison with the as-synthesized sample.
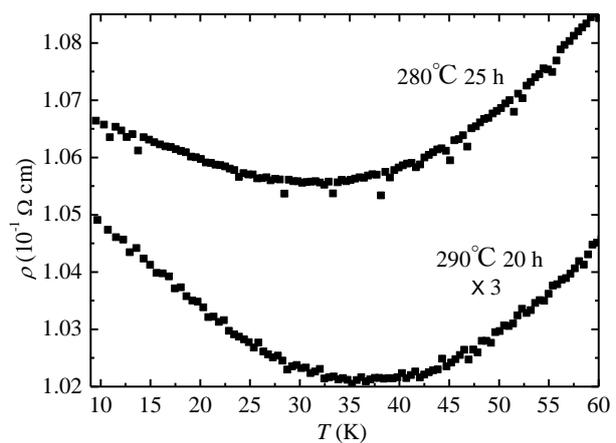
Fig. 5. Temperature dependence of ρ in the low-temperature range for the S-deintercalated samples of $Nd_{3.5}Sm_{0.5}Ni_3O_8$ with the conditions of 280 °C, 25 h and 290 °C, 20 h. The ρ of 290 °C 20 h sample is multiplied by a factor of 3 for easy comparison with other sample.

4. Conclusions

  In conclusion, it has been found that semiconducting behaviour is suppressed and that metallization may start at approximately 170 K by our high-pressure measurements for the as-synthesized sample. This suggests that the metallic transport properties are closely related to its antiferromagnetic fluctuations. The metallic samples have been successfully obtained by sulfur-intercalation and subsequent deintercalation without applying pressure. Very large values of ρ in the metallic state suggest that, like high-T_c cuprates, the transport mechanism in this system does not obey conventional Boltzmann transport theory. In the metallic samples, the ρ data suggest a weak semiconducting nature for $T < 35$ K. This may be due to randomness in the crystal, probably due to damage caused by the intercalation and deintercalation processes or by, chemical doping of Sm in the Nd sites. In addition, remnant additional oxygens may exist at the apical sites of Ni. The kinetic-energy gains of carriers caused by applying pressures up to 2 GPa are not sufficient to overcome the random potentials in the crystal. The deintercalation process must therefore be improved to suppress the effects of randomness. In band-structure calculations, the conduction band composed of Ni-$3d$ and O-$2p$ orbitals is 1~2 eV narrower than that of high-T_c cuprates [10-12]. The present system thus appears to be more sensitive to randomness than the high-T_c cuprates. In other words, the carriers tend to be localized more easily in the present system. In order to obtain superconductivity, it may be better to use the as-synthesized sample at pressures greater than 2 GPa, rather than using S-deintercalated samples, or to use $Nd_4Ni_3O_8$ without Sm doping to avoid the randomness.

References

[1] Y. Sakurai, N. Chiba, Y. Kimishima, and M. Uehara, Physica C **487**, 27 (2013).
[2] Y. Sakurai, S. Sakura, G, HU, S. Suzuki, I. Umehara, Y. Kimishima, and M. Uehara, JPS Conf. Proc. **1**, 012086 (2014).
[3] P. Lacorre, J. Solid State Chem. **97**, 495 (1992).
[4] R. Retoux, J. Rodriguez-Carvajal, and P. Lacorre, J. Solid State Chem. **140**, 307 (1998).
[5] V. V. Poltavets, K. A. Lokshin, S. Dikmen, M. Croft, T. Egami, and M. Greenblatt, J. Am. Chem. Soc. **128**, 9050 (2006).
[6] V. V. Poltavets, K. A. Lokshin, M. Croft, T. K. Mandal, T. Egami, and M. Greenblatt, Inorg. Chem. **46**, 10887 (2007).
[7] V. V. Poltavets, K. A. Lokshin, A. H. Nevidomskyy, M. Croft, T. A. Tyson, J, Hadermann, G. V. Tendeloo, T. Egami, G. Kotliar, N. ApRoberts-Warren, A. P. Dioguardi, N. J. Curro, and M. Greenblatt, Phys. Rev. Lett. **104**, 206403 (2010).
[8] N. ApRoberts-Warren, A. P. Dioguardi, V. V. Poltavets, M. Greenblatt, P. Klavins, and N. J. Curro, Phys. Rev. B **83**, 014402 (2011).
[9] V. V. Poltavets, M. Greenblatt, G. H. Fecher, and C. Felser, Phys. Rev. Lett. **102**, 046405 (2009).
[10] V. Pardo and W. E. Pickett, Phys. Rev. B **85**, 045111 (2012).
[11] V. Pardo and W. E. Pickett, Phys. Rev. Lett **105**, 266402 (2010).
[12] S. Sarkar, I. Dasgupta, M. Greenblatt, and T. Saha-Dasgupta, Phys. Rev. B **84**, 180411 (2011).
[13] J.-G. Cheng, J.-S.Zgou, J. B. Goodenough, H. D. Zhou, K. Matsubayashi, Y. Uwatoko, P. P. Kong, C. Q. Jin, W. G. Yang, and G. Y. Shen, Phys. Rev. Lett. **108**, 236403 (2012).
[14] A. Nakata, S. Yano, H. Yamamoto, S. Sakura, Y. Kimishima, and M. Uehara, Adv. Condens. Matter Phys. **2016**, 5808029 (2016).
[15] M. Imada, A. Fujimori, and Y. Tokura: Rev. Mod. Phys. **70**, 1039 (1998).
[16] J. Zhang, Y-S. Chen, D. Phelan, H. Zhang, M. R. Norman, and J. F. Mitchell, Proc. Natl. Acad. Sci. U.S.A. **113**, 8945 (2016).
[17] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989).