



ELSEVIER

Physica B 270 (1999) 332–340

PHYSICA B

Correlation between hopping conduction and transferred exchange interaction in $\text{La}_2\text{NiO}_{4+\delta}$ below 300 K

E. Iguchi^{a,*}, H. Satoh^a, H. Nakatsugawa^a, F. Munakata^b^a*Materials Science, Department of Mechanical Engineering and Materials Science, Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-Ku, Yokohama, 240-8501, Japan*^b*Nissan Research Centre, Nissan Motor Co., Ltd., 1 Natsushima-cho, Yokosuka, 237-8523, Japan*

Received 16 September 1998

Abstract

In order to investigate the correlation between electrical transport properties and the transferred exchange interaction between Ni^{2+} and La^{3+} in $\text{La}_2\text{NiO}_{4+\delta}$, bulk conductivities and dielectric properties of $\text{La}_2\text{NiO}_{4.02}$ and $\text{La}_2\text{NiO}_{4.125}$ have been measured as a function of temperature up to 300 K. The complex-plane impedance analyses determined bulk conductivities. Temperature dependencies of bulk conductivities, the self-consistent agreement of the energies obtained in the bulk conduction and dielectric relaxation processes, and the electron transferred integrals determined in dielectric measurements are indicative of the nonadiabatic hopping conduction, although the conductivity in $\text{La}_2\text{NiO}_{4.125}$ is very high with a very low hopping energy in comparison with $\text{La}_2\text{NiO}_{4.02}$. These results have been discussed in terms of the transferred exchange interaction between $\text{Ni}^{2+} 3d_{z^2}$ orbital and $\text{La}^{3+} 6s$ orbital through $2p_z$ orbital of apical O^{2-} . With increasing the content of excess oxygen, the decrease in the number of $\text{Ni}^{2+} 3d_{z^2}$ orbitals, which play an important role in the transferred exchange interaction, changes remarkably the conduction behaviour in $\text{La}_2\text{NiO}_{4.125}$ from $\text{La}_2\text{NiO}_{4.02}$. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 71.27. + a; 71.38. + i; 72.20 – i; 77.22.Gm

Keywords: $\text{La}_2\text{NiO}_{4+\delta}$; Electrical transport properties; Nonadiabatic hopping conduction; Transferred exchange interaction; Electronic structure; Complex-plane impedance analysis

1. Introduction

K_2NiF_4 -type $\text{La}_2\text{NiO}_{4+\delta}$ is the end member of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ system which was investigated extensively on the analogy of the high- T_c superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [1–5]. The natures and

properties of La_2NiO_4 and La_2CuO_4 are highly sensitive to the content of excess oxygen. In fact, $\text{La}_2\text{CuO}_{4+\delta}$ exhibits the metal–insulator transition at $\delta \cong 0.08$ [6] and bulk high- T_c superconductivity appears below T_c [7]. Though $\text{La}_2\text{NiO}_{4+\delta}$ remains semiconducting up to $\delta = 0.25$ [7], hole doping due to excess oxygen induces increasing structural distortion and changes electronic structures which modify the band gap width [8]. The main interest in La_2NiO_4 has been hole doping since the formal valence of Ni^{3+} created by hole doping could take

*Corresponding author. Tel.: + 81-45-339-3856; fax: + 81-45-331-6593.

E-mail address: iguchi@post.me.ynu.ac.jp (E. Iguchi)

a low-spin configuration with $S = \frac{1}{2}$ which is equivalent to the spin state of Cu^{2+} in the high- T_C superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [9–12]. The present study is, however, interested in electronic transport properties of electron-doped $\text{La}_2\text{NiO}_{4+\delta}$.

In $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ which undergoes a charge-ordering transition at $T_{CO} \cong 240$ K, the spectral changes with temperature above T_{CO} suggest fluctuating charged stripes or formation of small polarons [5]. $\text{La}_2\text{NiO}_{4+\delta}$ exhibits semiconducting behaviour at low temperatures with thermally activated or variable range hopping type of conductivity [3]. The transport properties in $\text{La}_{2-x}\text{NiO}_{4-\delta}$ at low temperatures are characteristic of adiabatic hopping conduction of localized carriers in the valence band tail above a mobility edge [8]. Though these previous experiments suggest a high possibility that the majority carrier at low temperatures in $\text{La}_2\text{NiO}_{4+\delta}$ is a polaron, the details of the transport kinetics are still unknown. Since the hopping process has a high probability of involving a dielectric relaxation as the carriers are excited from the potential wells associated with their self-trapping [13–21], the dielectric measurements could provide important knowledge on electrical conduction in $\text{La}_2\text{NiO}_{4+\delta}$. In order to correlate the charge dynamics (and/or polaron dynamics) with the electrical transport mechanism, a high-quality crystal is required because the ceramics specimens suffer from the carrier scattering in grain boundaries. The usage of single $\text{La}_2\text{NiO}_{4+\delta}$ crystals like Wada et al. [4], Freltoft et al. [22] and Yamada et al. [7,23] relieves most problems. Their single crystal results should be then referred to very carefully. Even if a polycrystalline ceramics specimen is employed, however, the complex-plane impedance analysis distinguishes the bulk conduction from the conduction across the grain boundary and the transport across the electrode-specimen interface, if they exist [24–26]. Then, the combination of the complex-plane impedance analysis and the dielectric measurement could be a very reliable means for the investigation of electrical transports in polycrystalline $\text{La}_2\text{NiO}_{4+\delta}$.

There is another aspect to consider in physics of $\text{La}_2\text{NiO}_{4+\delta}$, i.e., the transferred exchange interaction [27]. In La_2NiO_4 , Ni^{2+} ($3d^8$) is in the low-spin state [28] and both the e_g orbitals, i.e., $3d_{x^2-y^2}$ and

$3d_{z^2}$, are occupied by one hole with parallel spins ($S = 1$) [27]. The large internal field H_{int} at La sites in La_2NiO_4 observed in ^{139}La zero-field NMR experiments [4,27,29] requires the strong transferred exchange interaction between Ni^{2+} $3d_{z^2}$ orbital and La^{3+} $6s$ orbital through $2p_z$ orbital of apical O^{2-} [30] and consequently the strong covalency between Ni^{2+} and La^{3+} via O^{2-} must be involved in the bonding. Then the half-filled $3d_{z^2}$ orbital plays an important role in the transferred exchange interaction [27]. Hole doping creates Ni^{3+} ($3d^7$) with only the half filled $3d_{x^2-y^2}$ orbital and, consequently, the transferred exchange interaction between Ni^{3+} and La^{3+} is almost quenched [27]. Accordingly, the covalent component in the bonding must decay in the hole-doped specimens. Such a change in the bonding nature must modify cell parameters, particularly the lattice constant along the c -axis, and also must vary the electrical conduction considerably. Therefore, it is of great importance to investigate the correlation between the amount of Ni^{3+} and the natures such as electrical transport properties, lattice constants and so on in $\text{La}_2\text{NiO}_{4+\delta}$. Such a correlation is a very interesting issue to debate and the main subject in the present study.

The strength of the transferred exchange interaction between Ni^{2+} and La^{3+} in $\text{La}_2\text{NiO}_{4+\delta}$ depends upon the amount of Ni^{3+} ions. In order to investigate the correlation between the electronic conduction and the transferred exchange interaction, therefore, electrical transport properties have to be measured as a parametric function of the content of Ni^{3+} ions. To this end, several specimens with different components of excess oxygen are required. $\text{La}_2\text{NiO}_{4+\delta}$ prepared by the standard solid-state reaction method in air and annealed in oxygen is in the oxygen excess state, i.e., $\delta \cong 0.12$ [3,7,27]. The reduction of the amount of Ni^{3+} ions in $\text{La}_2\text{NiO}_{4.12}$ requires electron doping which is generally difficult in strongly correlated electron systems like La_2NiO_4 because of the strong electron–electron interaction. Despite this, several attempts of electron doping have been tried in this system [8,22]. Bassat et al. prepared $\text{La}_{2-x}\text{NiO}_{4+\delta}$ for electron-doped specimens [8]. Though their results are very important, the deficiency of La^{3+} ions interferes with the elucidation of the relationship

between the electrical transport properties and the transferred exchange interaction. In order to dope electrons, it looks the most plausible and most conventional means to anneal $\text{La}_2\text{NiO}_{4.12}$ in a reducing atmosphere such as flowing hydrogen gas.

From this point of view, the present study will prepare two specimens, i.e., $\text{La}_2\text{NiO}_{4.02}$ and $\text{La}_2\text{NiO}_{4.125}$, describe the experimental results of these specimens, discuss the kinetics of the conduction and the correlation between the electrical transport and the amount of Ni^{3+} referring to the difference in the experimental results of these specimens, and then speculate over the electronic structures and the transferred exchange interaction in $\text{La}_2\text{NiO}_{4+\delta}$.

2. Experimental

$\text{La}_2\text{NiO}_{4+\delta}$ polycrystalline ceramics specimen was prepared by the conventional solid state synthesis technique. La_2O_3 and NiO powders were used (4N). First, the mixed powder was calcined in air at 950°C for 1 day. After being ground and mixed well, the powder was heated again in air at 1000°C for 1 day. Then the powder was pressed into pellets and sintered finally in pure flowing oxygen at 1000°C for 12 h. CuK_α X-ray diffraction of this specimen showed a tetragonal single phase with the lattice constants, $a = 3.8615 \text{ \AA}$ and $c = 12.6484 \text{ \AA}$, which were in good agreement with the data in JCPDS (Code; #34-0314).

The ICP (induction-coupled plasma) analysis determines the atomic ratio of $[\text{La}]/[\text{Ni}] = 2/0.99$ which corresponds with the stoichiometric ratio, $[\text{La}]/[\text{Ni}] = 2/1$, within the experimental errors. The chemical analysis using the iodometric titration yields δ in $\text{La}_2\text{NiO}_{4+\delta} = 0.12 \pm 0.01$. Fig. 1 shows the temperature dependence of the magnetization for this specimen, which exhibits the sharp peak around 110 K. The magnetic susceptibilities, χ , were measured by a SQUID (Quantum Design, MPMS). According to the experiments by Yamada et al. [7], the best ordered incommensurate phase at $\delta = 1/8 = 0.125$ shows the sharp peak of the magnetization at $T_N = 110 \text{ K}$, where the Néel temperature, T_N , is determined by neutron diffraction measurements. Even if δ deviates very slightly from

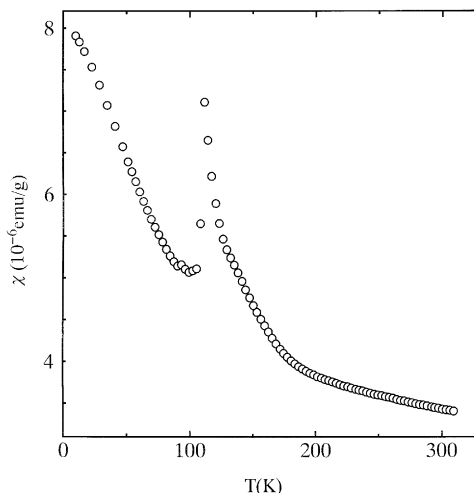


Fig. 1. χ versus T for $\text{La}_2\text{NiO}_{4.125}$.

0.125, the magnetization peak due to the anti-ferromagnetic transition decays remarkably and nearly disappears. The result of Yamada et al. [7] indicates the well-defined phase of $\delta = 0.125$ in the present specimen, i.e., $\text{La}_2\text{NiO}_{4.125}$ with the atomic ratio of $[\text{Ni}^{3+}]/[\text{Ni}^{2+}] = \frac{1}{3}$. This estimate for δ agrees with the iodometric titration result within the experimental errors. The density of the specimen was about 88% of the theoretical value.

In order to dope electrons, the specimen prepared in this way was moreover annealed in pure flowing hydrogen at 450°C for 7 h. The X-ray diffraction showed that this reduced specimen had an orthorhombic structure with the lattice constants, $a = 3.8644 \text{ \AA}$, $b = 3.9156 \text{ \AA}$ and $c = 12.5351 \text{ \AA}$. The remarkable reduction in the lattice constant along the c -axis is noteworthy. The iodometric titration analysis yields $\delta \cong 0.02 \pm 0.01$. Then, $\text{La}_2\text{NiO}_{4.02}$ is produced by the hydrogen reduction, which contains a negligibly small amount of Ni^{3+} ions.

Capacitance and impedance were obtained as a function of temperature by the four-terminal pair AC impedance measurement method, using an HP 4284A precision LCR meter with a frequency range of 100 Hz to 1 MHz. The measured values of capacitance and impedance were corrected by calibrating capacitance and resistance of leads to zero. Flat surfaces of the specimens were coated with an In–Ga alloy in 7:3 ratio by a rubbing technique for

an electrode. Evaporated gold was also used for the electrode but no significant difference was found in experimental results. A Maxwell–Wagner-type polarization due to heterogeneity in a specimen is excluded because there is no significant difference in the frequency dependency of dielectric constant at 200 K even if the thickness of the specimen is reduced to half.

A Keithley 619 resistance bridge, an Advantest TR 6871 digital multimeter and an Advantest R 6161 power supply were used for DC conductivity-measurements by the four-probe method. The copper–constantan pre-calibrated at 4.2, 77 and 273 K was used for the temperature measurements.

3. Results

Following the detailed account of the theoretical treatment [24–26], the complex-plane impedance analyses were carried out. Usually, in polycrystalline ceramics, three independent semicircular arcs show up in the impedance plots where the real part (Z') of the total impedance is plotted against the imaginary part (Z'') as a parametric function of frequency f , i.e., the highest frequency arc corresponding to the bulk conduction, the intermediate one due to the conduction across the grain boundary and the lowest frequency arc coming from the transport across the electrode–specimen interface. The resistance values of the circuit elements are obtained from the real axis intercepts. Fig. 2 depicts complex-plane impedance plots at 200 K for $\text{La}_2\text{NiO}_{4.02}$ and 55 K for $\text{La}_2\text{NiO}_{4.125}$. The solid line curves were determined by the least-mean-square analyses. The high conductivities in $\text{La}_2\text{NiO}_{4.125}$ enable the impedance analyses at remarkably low temperatures in comparison with $\text{La}_2\text{NiO}_{4.02}$. Since the lowest frequency arc was not observed in each specimen, there must be no electrode polarization in the electrode–specimen interface within the frequency range employed in the present work. The highest resistance value of the highest frequency arc is the resistance within grains. As for $\text{La}_2\text{NiO}_{4.125}$, the impedance analysis at $T > 160$ K requires frequencies higher than 1 MHz, the maximum frequency in the present study, while the impedance analysis at $T < 40$ K requires fre-

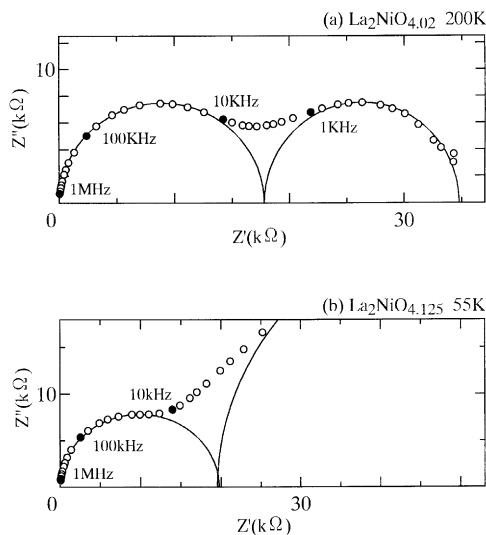


Fig. 2. The complex-plane impedance plots for (a) $\text{La}_2\text{NiO}_{4.02}$ at 200 K and (b) $\text{La}_2\text{NiO}_{4.125}$ at 55 K.

quencies lower than 100 Hz. Because of the similar reason, there is also the temperature region in which the impedance analysis is possible to carry out for $\text{La}_2\text{NiO}_{4.02}$.

Fig. 3 plots Arrhenius relations of $\sigma T^{3/2}$ and $1/T$ for both the specimens, where σ is the bulk conductivity obtained from the highest resistance value of the highest frequency arc. First of all, one should notice the big difference in conductivities between these specimens despite the small difference in δ of $\text{La}_2\text{NiO}_{4+\delta}$, i.e., $\Delta\delta = 4.125 - 4.02 \cong 0.1$. As well as other various oxides [19,21,31–34], the four-probe DC conductivities in these specimens overlapped conductivities estimated from the highest resistance values of intermediate frequency arcs, which were theoretically the total resistances in grains and boundaries [24–26]. At $T > 160$ K, there is a linear portion in $\text{La}_2\text{NiO}_{4.02}$ with an activation energy of 0.24 eV whereas $\text{La}_2\text{NiO}_{4.125}$ also involves the linear portion at $T > 60$ K with an activation energy of 0.083 eV. In both the specimens, conductivities deviate from the Arrhenius relations at lower temperatures.

In each specimen, a relaxation process shows up in dielectric loss tangent ($\tan \delta$) and electric modulus (imaginary part, M''), as shown in Fig. 4 which plots realistic loss tangent and electric modulus as

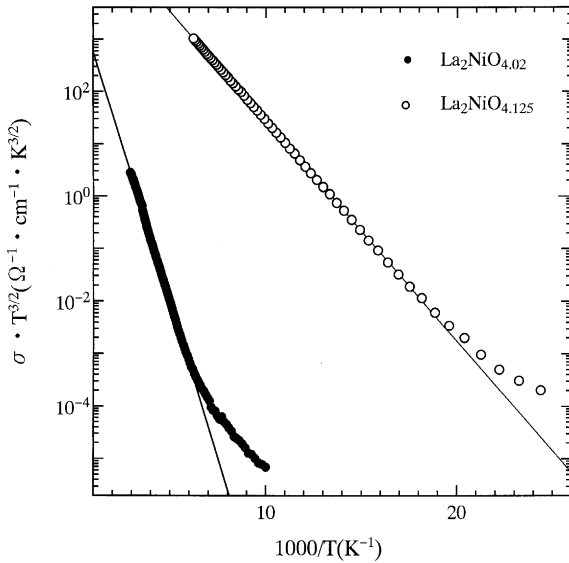


Fig. 3. Arrhenius relations of $\sigma T^{3/2}$ versus $1/T$ for $\text{La}_2\text{NiO}_{4.02}$ (solid circles) and $\text{La}_2\text{NiO}_{4.125}$ (open circles), where σ is the bulk conductivity obtained from the real axis intercept of the highest frequency arc in the impedance analysis.

a function of applied frequency at several temperatures for $\text{La}_2\text{NiO}_{4.02}$. The realistic dielectric loss tangent values are obtained by subtracting low-frequency contributions in the similar way to Lalevic et al. [35].

4. Discussion

4.1. Nonadiabatic hopping conduction

When small polarons are carriers predominantly responsible for conduction, they have the characteristic temperature dependencies of conductivities, i.e., $\sigma T^\gamma \propto \exp(-E/k_B T)$, $\gamma = 1$ for the adiabatic case and $\frac{3}{2}$ for the nonadiabatic case [36], where the dominant component of E is the hopping energy of small polarons, W_H [16–21,31–34]. The result in Fig. 3 seems surely to favour the polaronic scenario of the nonadiabatic case for both the specimens. This is ensured by the dielectric experiments.

The dielectric behaviour in Fig. 4 is described approximately by Debye's theory [37,38]. At a temperature T , the loss tangent and the electric

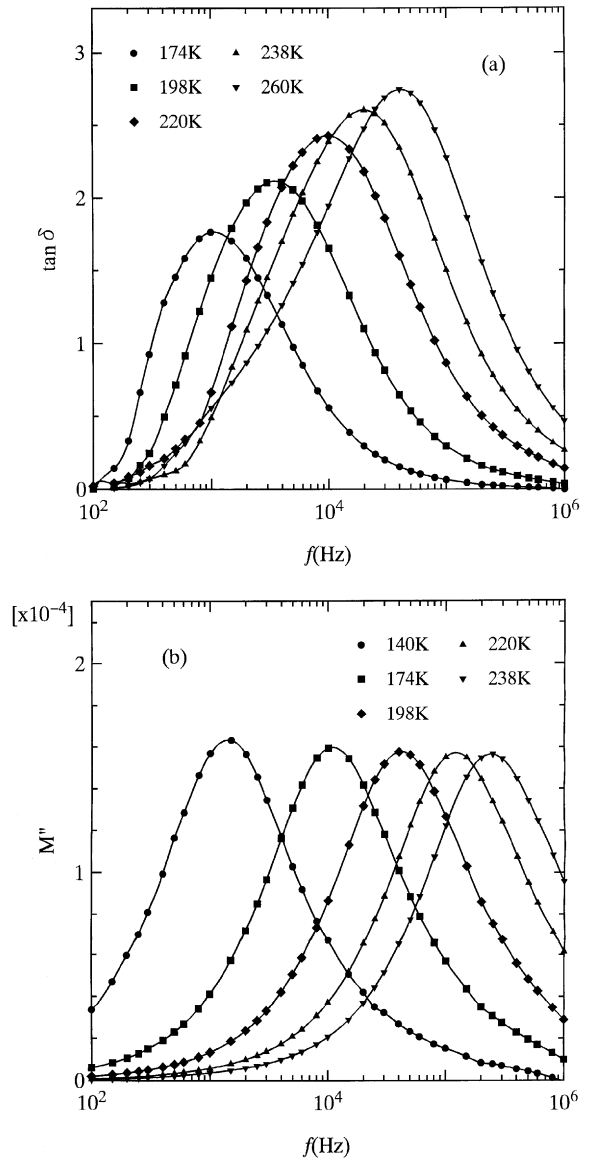


Fig. 4. (a) Frequency dependencies of loss tangent, $\tan \delta$, and (b) electric modulus (imaginary part), M'' , at several temperatures for $\text{La}_2\text{NiO}_{4.02}$.

modulus have maxima at the resonance frequencies, $f_{\tan \delta}$ and f_M , respectively, i.e., $(\tan \delta)_{\max} = (\epsilon_0 - \epsilon_\infty)/2\sqrt{\epsilon_0 \epsilon_\infty}$ at $f_{\tan \delta} = \sqrt{\epsilon_0/\epsilon_\infty}/2\pi\tau$ and $M''_{\max} = (\epsilon_0 - \epsilon_\infty)/2(\epsilon_0 \epsilon_\infty)$ at $f_M = (\epsilon_0/\epsilon_\infty)/2\pi\tau$, where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, and τ is the relaxation time at

T which has a form of $\tau = \tau_0 \exp(Q/k_B T)$, Q being the activation energy required for the dielectric relaxation. In the polaronic scenario, the activation energy is the hopping energy, i.e., $Q = W_H$ [16–21]. In the nonadiabatic case, $\tau_0 = 2\hbar(W_H k_B T)^{1/2} / \pi^{1/2} J^2$, where J is the electron transfer integral between the neighbouring hopping sites and \hbar is the Planck's constant divided by 2π [16,21,34,39,40].

Using the frequencies at the maxima of loss tangent and electric modulus, one has the relation $(f_{\text{tan}\delta})^2 T^{1/2} / f_M = [J^2 / 4\pi^{1/2} \hbar (W_H k_B)^{1/2}] \exp(-W_H / k_B T)$ [16,21,34,39,40]. For $\text{La}_2\text{NiO}_{4.02}$, Fig. 5 plots the Arrhenius relation of $(f_{\text{tan}\delta})^2 T^{1/2} / f_M$ and $1/T$ at $T > 180$ K, which yields $W_H = 0.19$ eV, while W_H is 0.069 eV for $\text{La}_2\text{NiO}_{4.125}$ which has the straight line at $T > 60$ K. The experimental values for $[J^2 / 4\pi^{1/2} \hbar (W_H k_B)^{1/2}]$ obtained by the extrapolation at $T \rightarrow \infty$ yields $J = 8.85 \times 10^{-5}$ and 3.99×10^{-5} eV for $\text{La}_2\text{NiO}_{4.02}$ and $\text{La}_2\text{NiO}_{4.125}$, respectively. These experimental J -values are subject to the nonadiabatic conditions [39,41], i.e., $J < 4W_H$ and $J < (W_H k_B T)^{1/4} (\hbar \omega_{\text{OL}})^{1/2}$, if the frequency of the longitudinal optical mode, ω_{OL} , is assumed to lie in the range $10^{13} - 10^{14} \text{ s}^{-1}$. This assumption is employed because the experimental ω_{OL} -values for the similar perovskite materials are in the range of $10^{13} - 10^{14} \text{ s}^{-1}$ [42,43], although the frequency values of these specimens are not yet available experimentally.

The activation energy required for the conduction due to a hopping process of small polarons is the sum of the hopping energy, W_H , and half the energy required to create a free polaron, W_O , i.e., $E = W_H + W_O/2$ [16–21]. The disordered energy is omitted here because this is, in general, negligibly small in crystalline bulks compared with W_H , even less than the experimental errors in the determination of W_H [44]. There is another dielectric relation which estimates the magnitude for W_O , i.e., $(\tan \delta)_{\text{max}}^2 T / M''_{\text{max}} \propto \exp(-W_O/2k_B T)$ [17–21]. As shown also in Fig. 5, the straight lines in Arrhenius relations of $(\tan \delta)_{\text{max}}^2 T / M''_{\text{max}}$ and $1/T$ yield $W_O/2 = 0.044$ and 0.014 eV for $\text{La}_2\text{NiO}_{4.02}$ and $\text{La}_2\text{NiO}_{4.125}$. The sum of the energies obtained independently in Fig. 5 is very close in values to the activation energy in Fig. 3 for each specimen.

The assessment like this meets definitely the requirements for the nonadiabatic hopping con-

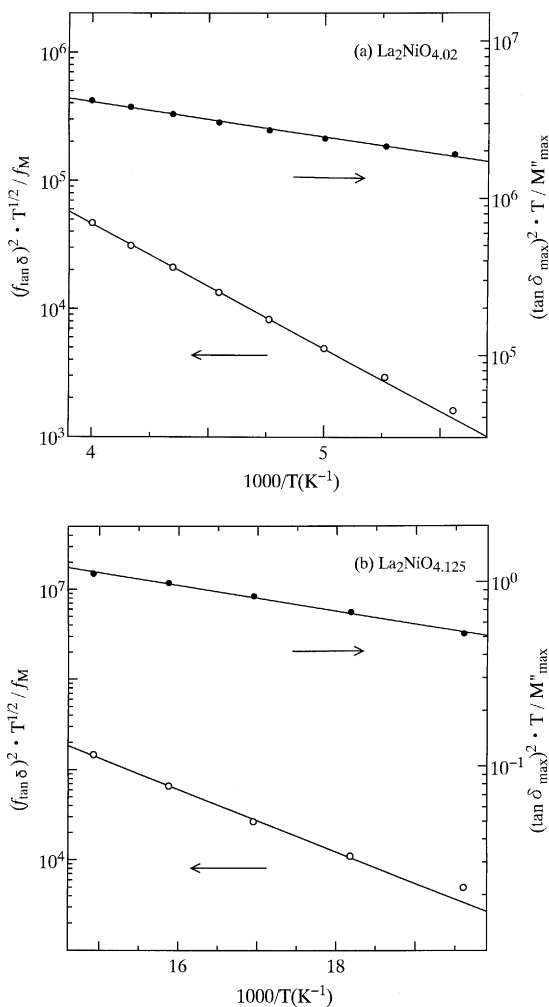


Fig. 5. Arrhenius relations between $(f_{\text{tan}\delta})^2 T^{1/2} / f_M$ and $1/T$ (open circles) and also between $(\tan \delta)_{\text{max}}^2 T / M''_{\text{max}}$ and $1/T$ (solid circles) for (a) $\text{La}_2\text{NiO}_{4.02}$ and (b) $\text{La}_2\text{NiO}_{4.125}$.

duction. Consequently the nonadiabatic Arrhenius plots in Fig. 3 are justified. The onset of non-Arrhenius bulk conduction at lower temperatures is found in each specimen. This is a general feature of small-polaron hopping. It arises when multiphonon jump processes are frozen out [45,46]. The conduction at lower temperatures is then described by an extension of the Arrhenius small-polaron hopping into the non-Arrhenius regime.

4.2. Electronic structures

$\text{Ni}^{2+}(3d^8)$ in $\text{La}_2\text{NiO}_{4.02}$ is in the low-spin state [28] and both the e_g orbitals are occupied by one hole with parallel spins ($S = 1$) [27]. Hole-doping by excess oxygen creates $\text{Ni}^{3+}(3d^7)$ in a low-spin configuration of $S = \frac{1}{2}$ with the half filled $3d_{x^2-y^2}$ orbital. The strong transferred exchange interaction between $\text{Ni}^{2+} 3d_{z^2}$ orbital and $\text{La}^{3+} 6s$ orbital through $\text{O}^{2-} 2p_z$ along the c -axis in $\text{La}_2\text{NiO}_{4.02}$ results in the tight covalent bonding nature which comes from the heavy hybridization of the wave functions of these ions. An increase in the amount of Ni^{3+} due to excess oxygen, however, weakens the transferred exchange interaction and then the covalent bonding component decays because the transferred exchange interaction between Ni^{3+} and La^{3+} is almost quenched as Furukawa et al. suggest [27]. Such a variation of the transferred exchange interaction describes well the relative magnitudes for the lattice constant along the c -axis in $\text{La}_2\text{NiO}_{4.02}$ and $\text{La}_2\text{NiO}_{4.125}$. The heavily hybridized wave functions due to the strong transferred exchange interaction in $\text{La}_2\text{NiO}_{4.02}$ lead to $c = 12.5351 \text{ \AA}$, considerably smaller than 12.6484 \AA of $\text{La}_2\text{NiO}_{4.125}$ which contains Ni^{3+} ions. Though excess oxygen at the tetrahedral site surrounded by La^{3+} between the double LaO_2 layers in $\text{La}_2\text{NiO}_{4.125}$ [47–49] contributes to such changes in the cell parameters to some extents, the remarkable reduction in the lattice constant along the c -axis compared with the lattice constants perpendicular to the c -axis is indicative of a strong relationship between the transferred exchange interaction and the electronic structure of Ni ion. Consequently, the change in the lattice constant along the c -axis in $\text{La}_2\text{NiO}_{4+\delta}$ system is mainly ascribed to the variation in the transferred exchange interaction caused by excess oxygen.

$\text{La}_2\text{NiO}_{4.125}$ has the very high conductivity with the low hopping energy compared with $\text{La}_2\text{NiO}_{4.02}$. Since the amount of Ni^{3+} ions is the density of 3d-type hole carrier, the conductivity in $\text{La}_2\text{NiO}_{4.125}$ with the atomic ratio of $[\text{Ni}^{3+}]/[\text{Ni}^{2+}] = \frac{1}{3}$ is very high compared with $\text{La}_2\text{NiO}_{4.02}$ which contains the negligibly small amount of Ni^{3+} . The 3d-hole type carriers, in general, heavily couple with extended wave functions

of O 2p-electrons, i.e., ligand holes [50–53]. Instead of the hybridization between $\text{Ni}^{2+} 3d_{z^2}$ and $\text{O}^{2-} 2p_z$ orbitals in $\text{LaNiO}_{4.02}$, then, another band must be formed by the hybridization of Ni unoccupied 3d orbital and O 2p orbital in $\text{La}_2\text{NiO}_{4.125}$. The neutron diffraction measurement by Yamada et al. detects the lattice modulation induced by the two-dimensional long-range hole order which predominantly occurs on NiO_2 planes in $\text{La}_2\text{NiO}_{4.125}$ [7]. The hybridization of the wave functions of the unoccupied 3d-state and the O 2p-state enables the charge-transfer on NiO_2 planes in the hole-ordered lattice. Since Ni^{2+} results in the strong transferred exchange interaction and Ni^{3+} nearly quenches this interaction [27], the interaction between Ni^{2+} and La^{3+} becomes progressively weak and instead the wave functions of Ni unoccupied 3d-state and O 2p-state are rapidly hybridized with increasing the amount of Ni^{3+} from $\text{La}_2\text{NiO}_{4.02}$. Such hybridization broadens the band width, t . There is the relationship between the hopping energy and the band width, i.e., $W_H = W_p/2 - t/2$, where W_p is the polaron binding energy [36,39]. In this context, the hopping energy in $\text{La}_2\text{NiO}_{4.125}$ is low as compared with $\text{La}_2\text{NiO}_{4.02}$. Then, in $\text{La}_2\text{NiO}_{4+\delta}$, there must be a correlation between the electrical conduction and the transferred exchange interaction.

Since the amount of Ni^{3+} is very small in $\text{La}_2\text{NiO}_{4.02}$, the electrical transport requires the creation of holes by the thermal excitation of electrons from the $e_{g\downarrow}$ levels to $e_{g\uparrow}$ in the low-spin states of Ni^{2+} ions. As shown in Fig. 4, the maximum of the loss tangent increases as temperature rises. This suggests the thermal excitation in the intensity of the dielectric relaxation which is proportional to the density of the carrier as well as other various materials in which hopping processes of small polarons dominate electrical transports [16,18,19,31,34,52,53]. The energy gap between $e_{g\downarrow}$ and $e_{g\uparrow}$ levels in $\text{La}_2\text{NiO}_{4.02}$ corresponds to the energy value obtained from the relation of $(\tan \delta)_{\max}^2 T / M_{\max}'' \propto \exp(-W_O/2k_B T)$, i.e., $W_O \cong 0.08 \text{ eV}$. As for $\text{La}_2\text{NiO}_{4.125}$, $W_O \cong 0.03 \text{ eV}$ which is about half the magnitude in $\text{La}_2\text{NiO}_{4.02}$, but in the same order. If the amount of mobile small polarons in $\text{La}_2\text{NiO}_{4.125}$ increases via the same excitation process as $\text{La}_2\text{NiO}_{4.02}$, hole-doping due to excess

oxygen modifies the energy gap width between $e_{g\downarrow}$ and $e_{g\uparrow}$ levels through the structural distortion and the change in electronic structures, as Bassat et al. suggest [8]. Besides this thermal excitation process, however, another interpretation is possible for $\text{La}_2\text{NiO}_{4.125}$. If small polarons of holes are trapped at imperfections like excess oxygen at very low temperatures, the energy required to release holes from imperfections is W_{O} . The similar process takes place very often in various oxides [16,18,34,52,53]. At the moment, however, it is unknown which process is more plausible in $\text{La}_2\text{NiO}_{4.125}$.

5. Conclusion

In order to investigate the correlation between electrical transport properties and the transferred exchange interaction between Ni^{2+} and La^{3+} along the c -axis in $\text{La}_2\text{NiO}_{4+\delta}$ system, two specimens have been prepared, i.e., $\text{La}_2\text{NiO}_{4.02}$ and $\text{La}_2\text{NiO}_{4.125}$. The bulk conductivities have been obtained by using complex-plane impedance analyses. These bulk conductivities follow the temperature dependency of the conduction due to a hopping process of nonadiabatic small polarons, i.e., $\sigma T^{3/2} \propto \exp(-E/k_{\text{B}}T)$, where the main component of E is the hopping energy of small polarons. $\text{La}_2\text{NiO}_{4.125}$ has the very high conductivity with the very low activation energy in comparison with $\text{La}_2\text{NiO}_{4.02}$. The nonadiabatic hopping conduction is ensured by the dielectric measurements because the sum of the hopping energy and half the energy to create a free nonadiabatic small polaron obtained in dielectric measurements is nearly equal to the energy required for the bulk conduction, and the electron transferred integral between the neighbouring hopping sites determined in the dielectric relaxation process is subject to the nonadiabatic conditions for each specimen.

The strong transferred exchange interaction between Ni^{2+} $3d_{z^2}$ orbital and La^{3+} $6s$ orbital through $2p_z$ orbital of O^{2-} in $\text{La}_2\text{NiO}_{4.02}$ becomes weak in $\text{La}_2\text{NiO}_{4.125}$ because Ni^{3+} ions induced by excess oxygen almost quench this interaction. The heavily hybridized wave functions of these ions due to this interaction reduce considerably the lattice constant along the c -axis in $\text{La}_2\text{NiO}_{4.02}$ com-

pared with $\text{La}_2\text{NiO}_{4.125}$. Being subject to the charge neutrality, Ni^{3+} ions due to excess oxygen in $\text{La}_2\text{NiO}_{4+\delta}$ system create 3d-hole type carriers. The high carrier density in $\text{La}_2\text{NiO}_{4.125}$ with $[\text{Ni}^{3+}]/[\text{Ni}^{2+}] = \frac{1}{3}$ is predominantly responsible for the high conductivity in this specimen compared with $\text{La}_2\text{NiO}_{4.02}$ which contains the negligibly small amount of Ni^{3+} . The 3d-holes heavily couple with extended wave functions of O $2p$ -electrons and then the bands between Ni unoccupied 3d orbital and O $2p$ orbital are formed. The increase in the amount of Ni^{3+} ions leads to the increase in the number of the bands, and then to the broadening of the band width, which reduces the hopping energy. These results are indicative of a strong correlation between the hopping conduction and the transferred exchange interaction in $\text{La}_2\text{NiO}_{4+\delta}$ system.

Acknowledgements

The authors are very grateful to N. Nakamura and K. Ueda for useful discussion and advice in this project. The chemical analyses were carried out by J. Noro. This project was supported by a Grant-in-Aid for Science Research (No. 08650812) from the Ministry of Education, Science and Culture, Japan, and Takahashi Industrial and Economic Foundation. The DC conductivities were measured at the Instrumental Analysis Centre in Yokohama National University. The SQUID magnetometer in Ecotechnology System Laboratory, Yokohama National University, was used.

References

- [1] R.J. Cava, B. Batlogg, T.T. Palstra, J.J. Krajewski, W.F. Peck Jr., A.P. Ramirez, L.W. Rupp Jr., Phys. Rev. B 43 (1991) 1229.
- [2] P. Kuiper, J. van Elp, G.A. Sawatzky, A. Fujimori, S. Hosoya, D.M. de Leeuw, Phys. Rev. B 44 (1991) 4570.
- [3] Th. Strangfeld, K. Westerholt, H. Bach, Physica C 183 (1991) 1.
- [4] S. Wada, Y. Furukawa, M. Kaburagi, T. Kajitani, S. Hosoya, Y. Yamada, J. Phys.: Condens. Matter 5 (1993) 765.
- [5] T. Katsufuji, T. Tanabe, T. Ishikawa, Y. Fukuda, T. Arima, Y. Tokura, Phys. Rev. B 54 (1996) R14230.

- [6] A. Demourgues, P. Dordor, J.P. Doumerc, J.C. Grenier, M. Marquestaut, M. Pouchard, A. Villesuzanne, A. Wattiaux, *J. Solid State Chem.* 124 (1996) 199.
- [7] K. Yamada, T. Omata, K. Nakajima, Y. Endoh, *Physica C* 221 (1994) 355.
- [8] J.M. Bassat, J.P. Loup, P. Odier, *J. Phys.: Condens. Matter* 6 (1994) 8285.
- [9] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, Y. Tokura, *Phys. Rev. B* 40 (1989) 2254.
- [10] J.B. Torrance, A. Bezing, A. Nazzal, T.C. Huang, S.S.P. Parkin, D.K. Keane, S.J. LaPlace, P.M. Horn, G.A. Held, *Phys. Rev. B* 40 (1989) 8872.
- [11] H. Rpmberg, M. Alexander, N. Nücker, P. Adelman, J. Fink, *Phys. Rev. B* 42 (1990) 8768.
- [12] S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, S. Tajima, *Phys. Rev. B* 43 (1991) 7942.
- [13] R. Gehlig, E. Salje, *Philos. Mag.* B 47 (1983) 229.
- [14] A. Mansingh, J.M. Reyes, M. Sayer, *J. Non-Cryst. Solids* 7 (1972) 12.
- [15] H.A.A. Sidek, I.T. Collier, R.N. Hampton, G.A. Saunders, B. Bridge, *Philos. Mag.* B 59 (1989) 221.
- [16] E. Iguchi, K. Akashi, *J. Phys. Soc. Japan* 61 (1992) 3385.
- [17] W.H. Jung, E. Iguchi, *Philos. Mag.* B 73 (1996) 873.
- [18] E. Iguchi, T. Hashimoto, S. Yokoyama, *J. Phys. Soc. Japan* 65 (1996) 221.
- [19] E. Iguchi, K. Ueda, W.H. Jung, *Phys. Rev. B* 54 (1997) 17431.
- [20] E. Iguchi, N. Nakamura, A. Aoki, *J. Phys. Chem. Solids* 58 (1997) 755.
- [21] E. Iguchi, N. Nakamura, A. Aoki, *Philos. Mag.* B 78 (1998) 65.
- [22] T. Freltoft, D.J. Buttrey, G. Aeppli, D. Vaknin, G. Shirane, *Phys. Rev. B* 44 (1991) 5046.
- [23] K. Yamada, T. Omata, K. Nakajima, S. Hosoya, T. Sumida, Y. Endoh, *Physica C* 191 (1992) 15.
- [24] J.R. MacDonald, *J. Chem. Phys.* 61 (1974) 3977.
- [25] J.R. MacDonald, *Superionic Conductors*, Plenum Press, New York, 1976, p. 1.
- [26] A.D. Franklin, *J. Am. Ceram. Soc.* 58 (1974) 127.
- [27] Y. Furukawa, S. Wada, *J. Phys.: Condens. Matter* 6 (1994) 8023.
- [28] G. Demazeau, J.L. Marty, B. Buffat, J.M. Dance, M. Pouchard, P. Dordor, B. Chevalier, *Mater. Res. Bull.* 17 (1982) 37.
- [29] Y. Furukawa, S. Wada, *J. Phys. Soc. Japan* 61 (1992) 1182.
- [30] M. Takahashi, T. Nishino, J. Kanamori, *J. Phys. Soc. Japan* 60 (1991) 1365.
- [31] E. Iguchi, K. Ueda, H. Nakatsugawa, *J. Phys.: Condens. Matter* (1998) in press.
- [32] W.H. Jung, H. Nakatsugawa, E. Iguchi, *J. Solid State Chem.* 133 (1997) 466.
- [33] W.H. Jung, E. Iguchi, *J. Phys. D* 31 (1998) 794.
- [34] E. Iguchi, H. Nakatsugawa, K. Futakuchi, *J. Solid State Chem.* 138 (1998) 176.
- [35] B. Lalevic, N. Fuschillo, B. Kuliyeu, W. Wang, *Apply. Phys.* 5 (1974) 127.
- [36] I.G. Austin, N.F. Mott, *Advanced Phys.* 18 (1969) 41.
- [37] H. Frölich, *Theory of Dielectric*, Clarendon Press, Oxford, 1958, p. 70.
- [38] R. Gehardt, *J. Phys. Chem. Solids* 55 (1994) 1491.
- [39] T. Holstein, *Ann. Phys. (NY)* 8 (1959) 343.
- [40] M.A. Kolber, R.K. MacCrone, *Phys. Rev. Lett.* 29 (1972) 1457.
- [41] D. Emin, *Phys. Rev. B* 4 (1971) 3639.
- [42] J.C. Phillips, *Physics of High- T_c Superconductors*, Academic Press, San Diego, 1989 (Chapter 4).
- [43] R. Raffaele, H.U. Anderson, C.D. Sparlin, D. Parris, *Phys. Rev. B* 43 (1991) 7991.
- [44] L.A.K. Dominik, R.K. MacCrone, *Phys. Rev.* 163 (1967) 756.
- [45] D. Emin, *Phys. Rev. Lett.* 32 (1974) 303.
- [46] D. Emin, *Phys. Today* 35 (1982) 34.
- [47] J.D. Jorgensen, B. Dabrowski, Shiyu Pei, D.G. Hinks, L. Soderholm, J.E. Striber, E.L. Venturini, D.S. Ginley, *Phys. Rev. B* 38 (1988) 11337.
- [48] J.D. Jorgensen, B. Dabrowski, Shiyu Pei, D.R. Richards, D.G. Hinks, *Phys. Rev. B* 40 (1988) 2187.
- [49] C. Chaillout, J. Chenavas, S.W. Cheong, Z. Fisk, M. Marezio, B. Morosin, J.E. Schirber, *Physica C* 170 (1990) 87.
- [50] M. Abbate, F.M.F. de Groot, J.C. Fuggle, A. Fujimori, O. Strebel, F. Lopez, M. Domke, G. Kaindl, G.A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki, S. Uchida, *Phys. Rev. B* 46 (1992) 4511.
- [51] M. Abbate, J.C. Fuggle, A. Fujimori, L.H. Tjeng, C.T. Chen, R. Potze, G.A. Sawatzky, H. Eisaki, S. Uchida, *Phys. Rev. B* 47 (1992) 16124.
- [52] W.H. Jung, E. Iguchi, *J. Phys. Soc. Japan* 63 (1994) 3078.
- [53] W.H. Jung, E. Iguchi, *J. Phys.: Condens. Matter* 7 (1994) 1995.