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The Electrical Properties of $La_{2-x}Sr_xNiO_4$ ($0\leqq x\leqq 1$)

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The electrical resistivities and Seebeck coefficients of mixed oxides, $La_{2-x}Sr_xNiO_4$, have been determined under an He atmosphere at 77.4—673.2 K. It has been shown that the temperature dependences of the Seebeck coefficients of the oxides were fairly well approximated by this equation: $S=AT+B+C/T$, where T is the thermodynamic temperature. The coefficients of the equation, A, B, and C, were given by the least-squares method. The metal-semiconductor ratios $\{\alpha\equiv(C/T)/(AT+C/T)\}$ were given to characterize the thermoelectrical properties of $La_{2-x}Sr_xNiO_4$. The maximal activation energies (E_a(resis.) and E_a(Seebeck)) and the maximal metal-semiconductor ratio (α) were obtained with the strontium concentration of $La_{2-x}Sr_xNiO_4$ at $x=0.5$. The lattice distortion of the oxides is responsible for the maxima of the activation energies and of the metal-semiconductor ratio at $x=0.5$.

The K_2NiF_4-type oxides are of great interest because of their unusual electrical properties. For example, La_2NiO_4 exhibits a gradual metal-semiconductor transition,[1–7] while $LaSrNiO_4$ is a metallic conductor[1,3,4] in the a axis direction of the tetragonal cell. The mixed oxides, La_2NiO_4 and $LaSrNiO_4$, form a continuous series of solid solutions,[3,4,8,9] $La_{2-x}Sr_xNiO_4$, which are also (tetragonal) K_2NiF_4-type oxides at $x=0$—1. Kononyuk et al.[3,4] have provided the resistivity and the thermoelectromotive force data of $La_{2-x}Sr_xNiO_4$. The measurements of the previous paper,[3,4] however, have been restricted to above room temperature; the data at temperatures below 300 K are not given.

In this paper, the electrical and transport properties of $La_{2-x}Sr_xNiO_4$ are reported in the range of 77.4—673 K, and the effects of lattice distortion on the electrical and transport properties are discussed.

Experimental

The mixed oxides, $La_{2-x}Sr_xNiO_4$, were prepared by heating a mixture of La_2O_3 (Shin-etsu Chem. Ind. Co., 99.9%), $SrCO_3$ (prepared from reagent grade $Sr(NO_3)_2$), and NiO (Koujundo Kagaku Co., 99.99%) in air at 1423 K for 20 h with intermittent grinding. The X-ray powder-diffraction method was employed for their identification.

Sintered specimens about 3 mm² in cross section and 10 mm long, which had been cut from pelletized samples 13 mm in diameter and 1 mm thick, were used for the electrical-resistivity and Seebeck-coefficient measurements.

Both four- and two-probe methods were employed for the resistivity measurements.

The Seebeck coefficients were determined by measuring the electric fields which were produced across a sintered bar of the specimen by the presence of temperature gradients. Two small copper blocks were employed for the potential leads. The temperature differences between the two potential leads were maintained within 15 K during the measurements.

The absolute Seebeck coefficients of the samples, S(abs.), were obtained by means of this equation:[10]

$$S(\text{abs.}) = S(\text{Cu}) - \Delta V/\Delta T, \tag{1}$$

where S(Cu) was the absolute Seebeck coefficient of copper[11] and where ΔV and ΔT were the potential and temperature differences between the two copper blocks respectively. All the resistivity and the Seebeck coefficient measurements were carried out under an He atmosphere.

Results and Discussion

The X-ray studies revealed that $La_{2-x}Sr_xNiO_4$ were tetragonal K_2NiF_4-type oxides over the entire range of x.[8]

The electrical resistivity measurements showed that all the sintered polycrystalline samples were semiconductors at room temperature (Fig. 1). In the series

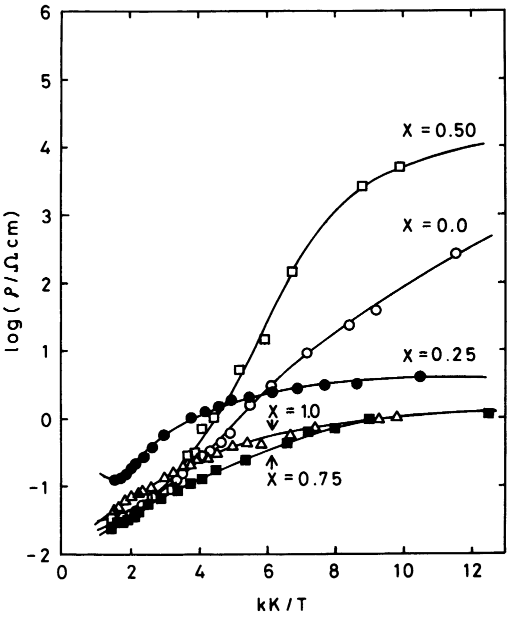

Fig. 1. Temperature dependence of electrical resistivity for $La_{2-x}Sr_xNiO_4$.

Table 1. Seebeck Coefficient and Activation Energy of $La_{2-x}Sr_xNiO_4$

$x^{a)}$	Temp range	Seebeck coefficient$^{b)}$			Activation energy$^{c)}$	
		A	B	C	E_a(resis.)	E_a(Seebeck)
	K	10^{-8} VK^{-2}	10^{-5} VK^{-1}	10^{-3} V	eV	eV
0.00	169—551	6.24	−4.80	8.91	0.081	0.009
0.25	146—619	2.93	−2.91	5.82	0.089	0.006
0.50	128—557	3.22	−5.22	11.2	0.097	0.011
0.75	110—506	−1.90	−0.93	1.78	0.052	0.002
1.00	91—607	−2.27	−0.19	0.56	0.072	<0.001

a) x in $La_{2-x}Sr_xNiO_4$. b) Seebeck coefficient at 300 K. $S=AT+B+C/T$. c) $\rho=\rho_0\exp(E_a(\text{resis.})/kT)$; $S=C/T=(k/e)(E_a(\text{Seebeck})/kT)$.

of $La_{2-x}Sr_xNiO_4$, a maximum value of the activation energy,

$$\rho=\rho_0\exp(E_a/kT), \qquad (2)$$

was obtained from the slope of the resistivity curve of $La_{1.5}Sr_{0.5}NiO_4$[3,4] (Table 1). A gradual metal-semiconductor transition was found in the resistivity curves of La_2NiO_4 and $La_{1.75}Sr_{0.25}NiO_4$ around 500 K.[1-7,9]

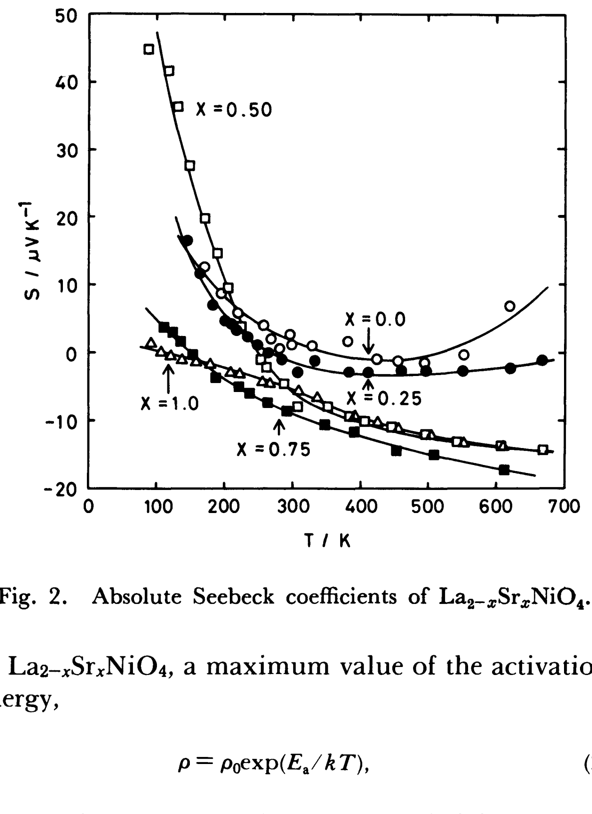

Fig. 2. Absolute Seebeck coefficients of $La_{2-x}Sr_xNiO_4$.

The thermo-electromotive force data (Fig. 2) suggested that $LaSrNiO_4$ was a metallic conductor,[1,3,4] but the resistivity data (Fig. 1) indicated that $LaSrNiO_4$ was a semiconductor with small activation energy. Charge transport among the grains across the boundary is probably responsible for the semiconduction of the polycrystalline $LaSrNiO_4$.

Goodenough[5,6] has proposed a band model of La_2NiO_4 in which the conduction band, a narrow $\sigma^*_{x^2-y^2}$ band, is split into two bands by either electron correlations or a charge-density wave; the lower band of the two is fully occupied by electrons, whereas the higher one is empty. It is safe to assume that $La_{2-x}Sr_xNiO_4$ have essentially the same energy-band structure as that of La_2NiO_4, since the crystal structures of La_2NiO_4 and $La_{2-x}Sr_xNiO_4$ are identical.

The $La_{2-x}Sr_xNiO_4$ oxides contain x Ni^{3+} cations per formula. If $La_{2-x}Sr_xNiO_4$ have the same energy band as La_2NiO_4, $La_{2-x}Sr_xNiO_4$ must be metallic conductors at any x except at $x=1$, even at low temperatures, since x holes do exist in $La_{2-x}Sr_xNiO_4$. Metallic conduction, however, was not observed in the series of $La_{2-x}Sr_xNiO_4$ except for $LaSrNiO_4$ in either Kononyuk's[3,4] and the present work at room temperature. This phenomenon can be understood if the nickel 3d holes are trapped around Sr^{2+} and are in the collective state, because Sr^{2+} is more negative than La^{3+}. In $La_{2-x}Sr_xNiO_4$, many donors, that is, acceptors of holes, should exist in the lower band of La_2NiO_4, and the conduction band of La_2NiO_4 must be deformed by Sr^{2+}.

So many Sr^{2+} and Ni^{3+} should also influence the transport properties of $La_{2-x}Sr_xNiO_4$. Thermo-electromotive force measurements showed that the Seebeck coefficients of $La_{2-x}Sr_xNiO_4$, except for La_2NiO_4 and $La_{1.75}Sr_{0.25}NiO_4$, decreased with an increase in the temperature over the entire range of measurements (Fig. 2). The Seebeck coefficient curves of La_2NiO_4 and $La_{1.75}Sr_{0.25}NiO_4$, however, had minima at around 500 K, where metal-semiconductor transitions were observed. All oxides were p-type conductors at low temperatures, but they were n-type above moderate temperatures.

In general, the Seebeck coefficient of a metallic conductor can be represented by this relation:

$$S=AT+B, \qquad (3)$$

where A and B are constants and where T is the thermodynamic temperature. On the other hand, the Seebeck coefficient of a semiconductor is expressed as:

$$S=C/T, \qquad (4)$$

where C is a constant. In the case of an intrinsic semiconductor, Eq. 4 can be altered as:

$$S=(k/e)(E_a/kT), \tag{5}$$

where k is the Boltzmann constant, e is the electronic charge, and E_a is the activation energy.

The Seebeck coefficient curves of the sintered samples of $La_{2-x}Sr_xNiO_4$ (Fig. 2) were complicated and could not be expressed simply by either Eqs. 3 or 4. Since the oxides were electrically anisotropic and both La_2NiO_4 and $La_{1.75}Sr_{0.25}NiO_4$ exhibit a "gradual" metal-semiconductor transition (Fig. 1), we hypothetically assumed that the metallic conduction and the semiconduction parts of the thermo-electromotive force, viz., $AT+B$ and C/T, coexist in the polycrystalline samples of $La_{2-x}Sr_xNiO_4$ and that their Seebeck coefficient consists of the sum of the two parts. The Seebeck coefficient of $La_{2-x}Sr_xNiO_4$ can, then, be written as:

$$S=AT+B+C/T. \tag{6}$$

This equation can also be written in this form:

$$ST=AT^2+BT+C. \tag{7}$$

The coefficients A, B, and C were evaluated by fitting the experimental measurements to Eq. 7 with a digital computer, using the least-squares method.

In Fig. 3 the observed and calculated products, ST, are plotted as a function of the temperature. The solid lines represent the calculated values (ST(calcd)$=AT^2+BT+C$). The calculations by the least-squares method were employed to obtain the thermo-electromotive force data at high temperatures (Table 1). The calculated values were in fair agreement with the values found for most of the temperature region. However, large deviation of the observed ST values from the calculated lines, which were greater than the limits of experimental error (±2 mV), were found in the low-temperature p-type regions of La_2NiO_4, $La_{1.75}Sr_{0.25}NiO_4$, and $La_{1.5}Sr_{0.5}NiO_4$. Unfortunately, it was not elucidated from our experimental data why the ST values of the samples ($x\leqq0.5$) deviated from the calculated ST curves at low temperatures.

In Fig. 4 the A and C coefficients are plotted as a function of the strontium concentration, x. The A coefficient was positive at $x\leqq0.6$ and negative at $x>0.6$. On the other hand, the C coefficient was positive over the whole range of x and increased with an increase in x. Figure 4 shows that both holes ($A\geqq0$ at $x<0.6$) and electrons ($A<0$ at $x>0.6$) were involved in the metallic conduction and that the holes were responsible for the semiconduction ($C\geqq0$ at $x=0$—1).

We attempted to seek a parameter (or a function) which contained the thermo-electromotive force data, i.e., A, B, and C, and which was related to the resistivity data. As has been described previously, the A and B coefficients were correlated with the metallic conduction, while the C parameter was correlated with the semiconduction. The thermo-electromotive force, AT, and C/T were temperature-dependent, and their values were determined by the sign, the density, and the mobility of the charge carriers in the energy band, while the residual power, B, was temperature-independent and it was usually difficult to predict its value. It seemed inappropriate to compare the values of A and/or C with B, since the value of B was unpredictable. Therefore, the B coefficient was ignored in evaluating the parameter (or the fucncton) in this paper.

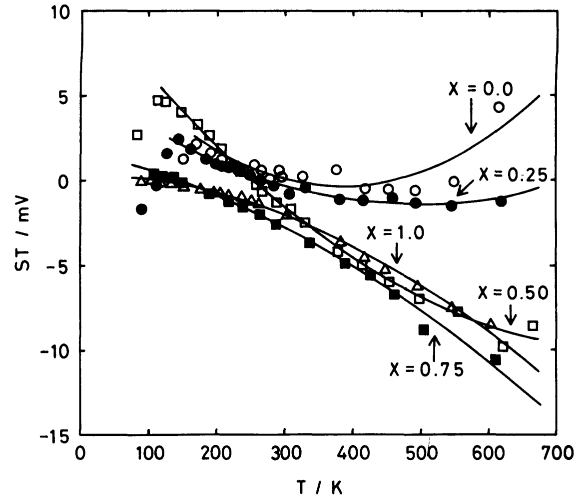

Fig. 3. ST vs. T plots of $La_{2-x}Sr_xNiO_4$.
The solid lines indicate the calculated values.

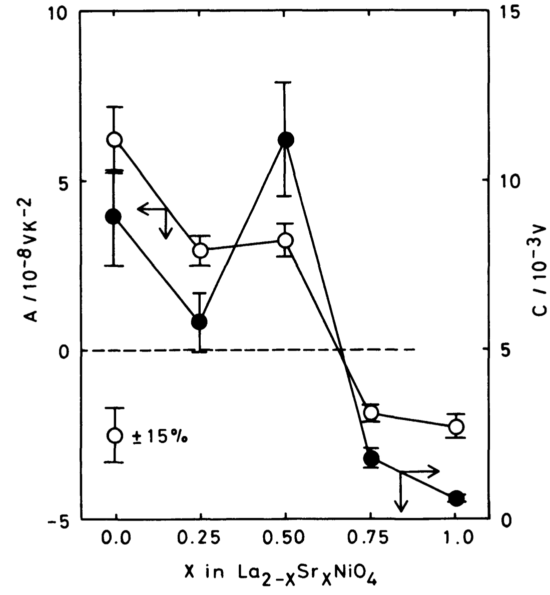

Fig. 4. The A and C values of $La_{2-x}Sr_xNiO_4$.
$S=AT+B+C/T$

The papprameter (or the function) was conveniently

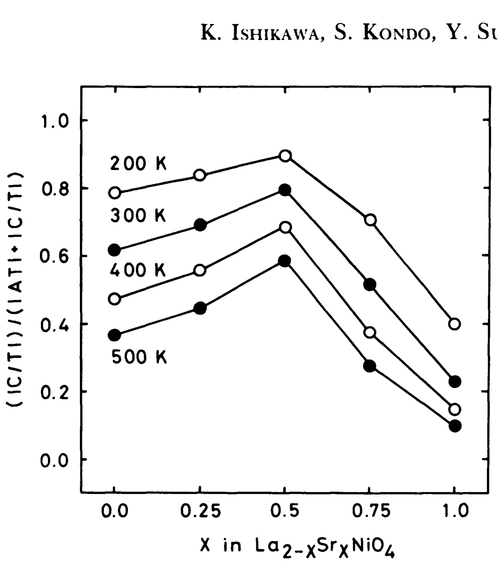

Fig. 5. The $(C/T)/(AT+C/T)$ values of La$_{2-x}$Sr$_x$NiO$_4$. $S=AT+B+C/T$

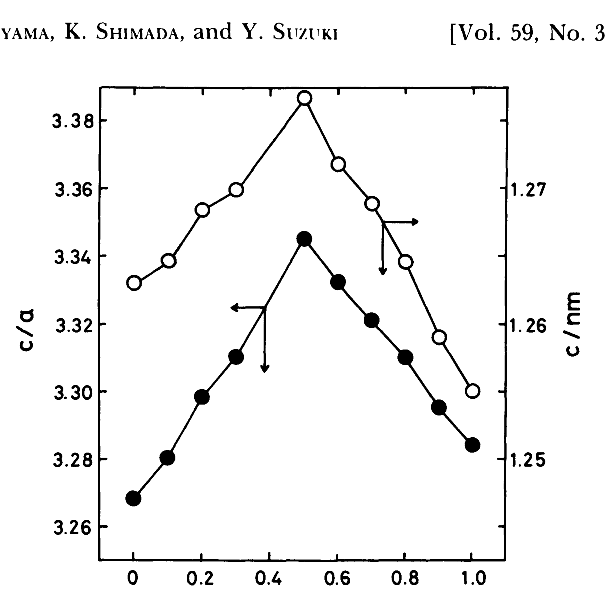

Fig. 6. Strontium concentration dependence of the c value and the c/a ratio of La$_{2-x}$Sr$_x$NiO$_4$ at 300 K. The lattice constants a and c were obtained from Gopalakrishnan et al.[8]

defined as the ratio of AT (metallic conductor) and C/T (semiconductor) as:

$$\alpha = \frac{C/T}{AT + C/T} \,. \tag{8}$$

The α parameter was named the metal-semiconductor ratio of the thermo-electromotive force.

In Fig. 5 the metal-semiconductor ratio of the oxides is plotted as a function of the strontium concentration. The metal-semiconductor ratio of the oxides decreased with an increase in the temperature. The ratio increased with x at $x<0.5$, but it decreased with x at $x\geqq 0.5$ at any temperature. Ganguly and Rao[1] and Kononyuk et al.[4] have reported that La$_2$NiO$_4$ showed a metal-semiconductor transition at 500 K and that LaSrNiO$_4$ was a metallic conductor. The metal-semiconductor ratio of La$_2$NiO$_4$ was 0.4 at 500 K, while that of LaSrNiO$_4$ was 0.2 at room temperature (Fig. 5). The metal-semiconductor transition seemed to occur at a critical value of $\alpha=0.3\pm0.1$. The La$_{1.5}$Sr$_{0.5}$NiO$_4$ oxide exhibited no metal-semiconductor transition because the metal-semiconductor ratio of the oxide was appreciably larger than the critical value in the temperature range measured.

In Fig. 6 the c/a and c values at room temperature of La$_{2-x}$Sr$_x$NiO$_4$, where a and c are the lattice constants of the tetragonal cell obtained from Gopalakrishnan et al.,[8] are plotted as a function of the strontium concentration. The shape of the metal-semiconductor ratio against the strontium-concentration curve in Fig. 5 very much more closely resembles the c vs. x curve than the c/a vs. x one.

In Table 1 the activation energies obtained from the resistivity data (E_a (resis.))(Eq. 2) and the activation energies calculated from the thermo-electromotive force data (E_a(Seebeck))(Eq. 5) are tabulated. The activation energies, E_a(Seebeck), are given merely as references, because the E_a(Seebeck) energies have some ambiguity which result from assuming that La$_{2-x}$Sr$_x$NiO$_4$ are intrinsic semiconductors. The activation energy (E_a(resis.)) and E_a(Seebeck) both had maxima at $x=0.5$. The activation energies must also be responsible for the crystal distortion.[5,6] The results in Figs. 5 and 6 and Table 1 indicate that the activation energy, as well as metal-semiconductor ratio of La$_{2-x}$Sr$_x$NiO$_4$, is correlated to the lattice distortion of the crystal.

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