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Na-site substitution effects on the thermoelectric properties of $NaCo_2O_4$

T. Kawata, Y. Iguchi, T. Itoh, and K. Takahata
Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan

I. Terasaki*
Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan
and Precursory Research for Embryonic Science and Technology, Japan Science Technology, Tokyo 102-0074, Japan

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The resistivity and thermopower of $Na_{1+x}Co_2O_4$ and $Na_{1.1-x}Ca_xCo_2O_4$ are measured and analyzed. In $Na_{1+x}Co_2O_4$, whereas the resistivity increases with x, the thermopower is nearly independent of x. This suggests that the excess Na is unlikely to supply carriers, and decreases effective conduction paths in the sample. In $Na_{1.1-x}Ca_xCo_2O_4$, the resistivity and the thermopower increase with x, and the Ca^{2+} substitution for Na^+ reduces the majority carriers in $NaCo_2O_4$. This means that they are holes, which is consistent with the positive sign of the thermopower. Strong correlation in this compound is evidenced by the peculiar temperature dependence of the resistivity. [S0163-1829(99)00536-6]

There appears a growing interest to a hunt for new thermoelectric (TE) materials,[1] reflecting urgent needs for a new energy-conversion system in harmony with our environments. A TE material generates electric power in the presence of temperature gradient through the Seebeck effect, and pumps heat in the presence of electric current through the Peltier effect. A serious drawback is the low conversion efficiency: It is characterized by the so-called ''figure of merit'' $Z=S^2/\rho\kappa$, where S, ρ, and κ are the thermopower, resistivity and thermal conductivity of a TE material, respectively. In other words, a good TE material is a material that shows large S, low ρ and low κ. However, a high value of Z is difficult to realize, because the three parameters cannot be changed independently. To overcome this difficulty, a number of new concepts and new materials have been examined.

Recently, we have observed that a layered cobalt oxide $NaCo_2O_4$ exhibits unusually large S (100 μV/K at 300 K) accompanied by low ρ (200 $\mu\Omega$cm at 300 K) along the direction parallel to the CoO_2 plane.[2] $NaCo_2O_4$ belongs to a layered Na bronze Na_xCoO_2, which was studied as a cathode for sodium batteries.[3] During the characterization, Molenda *et al.*[4] first found a large S in $Na_{0.7}CoO_2$. Although they noticed that S was anomalously large, they did not mention a possibility for a TE material. Their samples were polycrystals, the resistivity of which was 2–4 mΩcm at 300 K, much higher than that of our crystals. Our finding is that the carrier density (n) is of the order of 10^{21}–10^{22} cm^{-3}, and is two orders of magnitude larger than n of conventional TE materials. This is difficult to understand in the framework of a conventional one-electron picture, and may indicate a way to get a good TE material other than the conventional approach. We have proposed that strong electron-electron correlation plays an important role in the enhancement of the thermopower of $NaCo_2O_4$.

Even in a correlated system, we can expect that a conductor of low n will have a large S, because the diffusive part of S is the transport entropy, of the order of k_BT/E_F, where E_F is the Fermi energy.[5] Thus it would be tempting to improve the TE properties in $NaCo_2O_4$ by decreasing n. We easily think of three ways to change n in $NaCo_2O_4$, i.e., (i) doping of excess Na^+, (ii) the substitution of Ca^{2+} for Na^+, and (iii) the change of the oxygen content. Among them, we will discard the idea of (iii), because it will seriously deteriorate the conduction paths consisting of Co and O. Here, we report on the resistivity and thermopower of $Na_{1+x}Co_2O_4$ and $Na_{1.1-x}Ca_xCo_2O_4$ to study the doping effects.

We prepared polycrystalline samples of $Na_{1+x}Co_2O_4$ and $Na_{1.1-x}Ca_xCo_2O_4$ by solid-state reaction. Since Na is volatile, we added 10% excess Na. Namely we expected the starting composition of $Na_{1.1}Co_2O_4$ to be $NaCo_2O_4$. An appropriate mixture of Na_2CO_3, $CaCO_3$, Co_3O_4 was thoroughly ground, sintered at 860–920 °C for 12 h in air. The sintered powder was then pressed into a pellet, and sintered again at 800–920 °C for 6 h in air.

The x-ray diffraction (XRD) was measured using a standard diffractometer with Fe K_α radiation as an x-ray source in the $\theta-2\theta$ scan mode. Note that Cu K_α radiation is not suitable for this compound, because it emits the fluorescent x-ray of Co to make a high noise in the XRD pattern. ρ was measured through a four-probe method, in which the electric contacts with a contact resistance of 1Ω were made with silver paint (Dupont 4922). S was measured using a steady-state technique. Temperature gradient ($\sim$0.5 K/cm) was generated by a small resistive heater pasted on one edge of the sample, and was monitored by a differential thermocouple made of copper-constantan. A thermopower of voltage leads was carefully subtracted. Temperature (T) was controlled from 4.2 to 300 K in a liquid He cryostat, and was monitored with a CERNOX resistance thermometer.

Figure 1 shows typical XRD patterns of the prepared samples. Almost all the peaks are indexed as the P2 phase reported by Jansen and Hoppe,[6] though a tiny trace of impurity phases is detected as marked with * in Fig. 1. Note that all the XRD patterns are nearly the same, which means that XRD is not very powerful for the sample characterization. Thus the best way to characterize the samples is to measure their thermoelectric properties directly. Usually an impurity phase including Na will be Na_2O, and exist as deliquesced NaOH (Na_2O+H_2O). We think, however, that Na_2O is not a

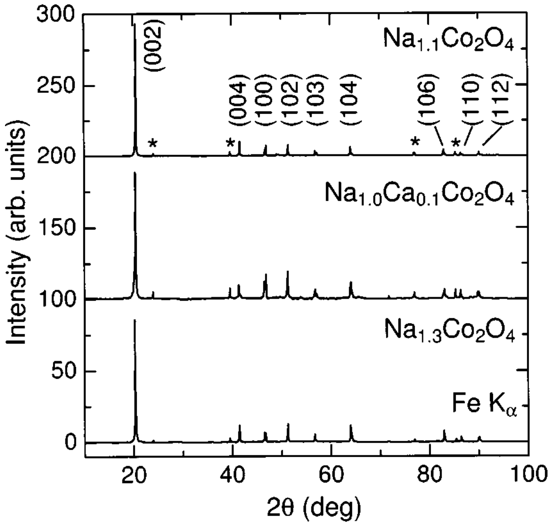

FIG. 1. The x-ray diffraction patterns of $Na_{1.1}Co_2O_4$, $Na_{1.3}Co_2O_4$, and $Na_{1.0}Ca_{0.1}Co_2O_4$. The Fe K_α radiation is used as an x-ray source. Most of the peaks are indexed as the P2 phase, while a few peaks of impurity phases are marked with *.

major impurity phase for the present case. The samples are stable enough to handle in air, and the contact resistance and the surface do not deteriorate against several-hour exposure to the air.

Figure 2(a) shows ρ for $Na_{1+x}Co_2O_4$ plotted as a function of T. Both the magnitude and the T dependence are consistent with previous studies.[4,7] All the samples show a metallic conduction down to 4.2 K without any upturn at low temperatures. This suggests that the conduction paths are not disturbed by the doped excess Na. The T dependence of ρ roughly resembles the in-plane resistivity for single-crystal $NaCo_2O_4$,[2] implying that the conduction of polycrystals is mainly determined by the in-plane conduction. Note that ρ for $x=0$ is higher than ρ for $x=0.1$, which suggests that a small amount of Na is evaporated through the sintering process.

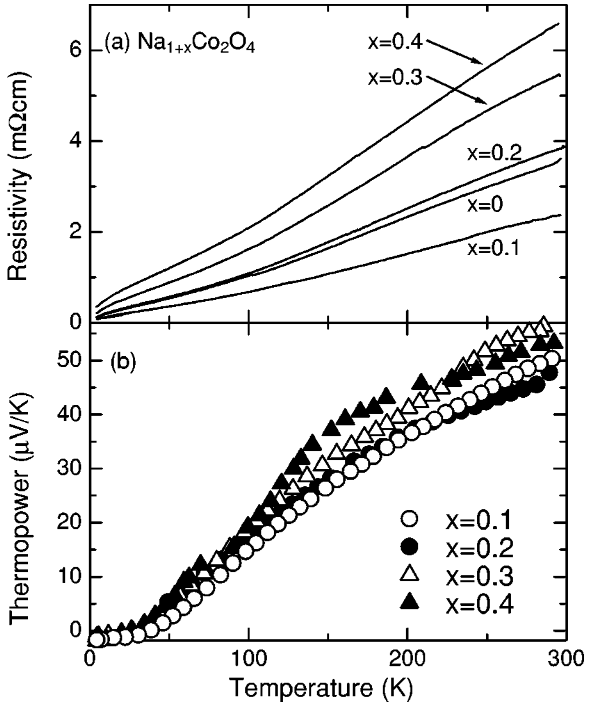

FIG. 2. (a) Resistivity and (b) thermopower of $Na_{1+x}Co_2O_4$ plotted as a function of temperature.

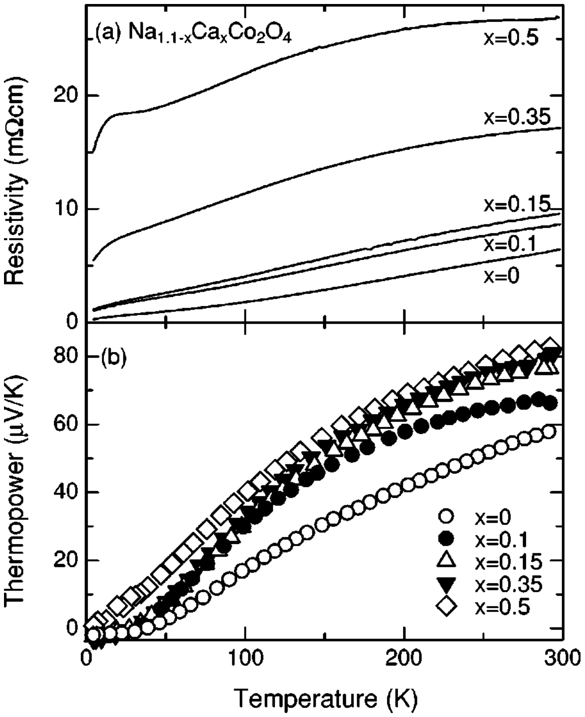

FIG. 3. (a) Resistivity and (b) thermopower of $Na_{1.1-x}Ca_xCo_2O_4$ plotted as a function of temperature.

Contrary to the change of ρ with x, S for $Na_{1+x}Co_2O_4$ is nearly independent of x as shown in Fig. 2(b). This indicates that n remains intact by doping Na. It is, at first sight, unusual why the doped monovalent Na^+ does not change n. We point out two possibilities: One is that the excess Na is excluded from the crystal to increase the resistance at the grain boundary, and the other is that it is in the grain to make an insulating phase nearby. Note that $NaCoO_2$ (corresponding to $x=1$) is an insulator.[3] In both cases, excess Na cations decrease the number of conduction paths to reduce the effective cross section for the current.

Making a remarkable contrast to Fig. 2(a), Fig. 3 (a) shows a drastic change of ρ for $Na_{1.1-x}Ca_xCo_2O_4$ with x. Above 50 K, while ρ for $x=0$ shows a positive curvature, ρ for $x=0.35$ shows a negative curvature to saturate near 300 K. Unlike the case of the excess Na, the residual resistivity, though not well defined, tends to increase with x, which means that Ca acts as a scattering center. S is also increased with x as shown in Fig. 3(b). Considering that both ρ and S increase with Ca, we conclude that the substitution of Ca^{2+} for Na^+ decreases the carriers. Namely the majority carrier of $NaCo_2O_4$ is a hole, which is consistent with the transport properties of $Na_{0.7}CoO_{2-\delta}$.[4] As expected, the TE properties are (slightly) improved by decreasing n, and S^2/ρ is maximized at $x=0.15$.

One may notice that $Na_{1.1}Co_2O_4$ shows different ρ between Figs. 2 and 3. The magnitude of ρ was scattered from batch to batch, possibly because the control of the grain growth is difficult. (Thermopower is a quantity less affected by grain boundaries, and the measured S was independent of

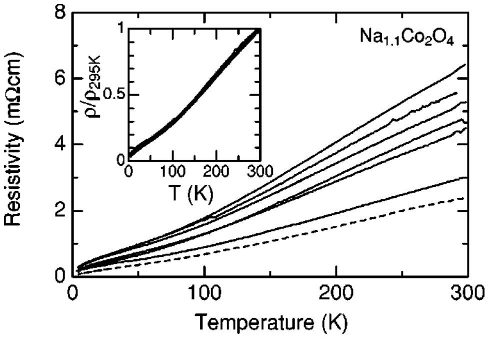

FIG. 4. Resistivity of $Na_{1.1}Co_2O_4$ prepared in different batches. The solid curves represent samples sintered at 860 °C, and the dashed curve represents a sample sintered at 920 °C. The magnitude of resistivity is scattered beyond experimental errors ($\sim$10%). The resistivity normalized at 295 K is shown in the inset.

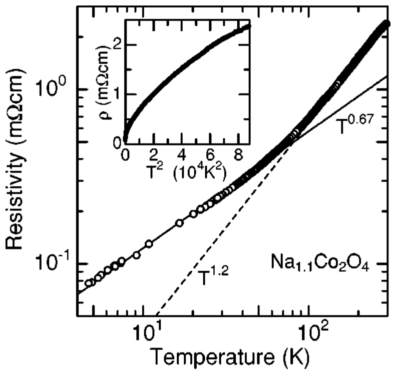

FIG. 5. Log-log plot of the resistivity of $Na_{1.1}Co_2O_4$. The data are the same as in Fig. 2(a). The solid and dashed lines represent $\rho\propto T^{0.67}$ and $\rho\propto T^{1.2}$, respectively. The inset shows ρ plotted as a function of T^2.

batches within experimental errors.) To see the reproducibility we made $Na_{1.1}Co_2O_4$ as a reference at every preparation run. Figure 4 shows ρ for $Na_{1.1}Co_2O_4$ prepared in different runs, where the magnitude of ρ is scattered beyond experimental errors ($\sim$10%). We note that the relative change of ρ among the same batch is reproducible, and the T dependence is essentially identical from batch to batch. All the $\rho-T$ data in Fig. 4 normalized at 295 K fall into a single curve, as shown in the inset of Fig. 4.

Figure 5 shows ρ of $Na_{1.1}Co_2O_4$ in Fig. 2(a) is plotted in a log-log scale. Since ρ is linear below 50 K and above 80 K, ρ is proportional to T^p in the two regions. From fitting ρ by T^p, we estimated p to be 0.67 below 50 K and 1.2 above 80 K (see the solid and dashed lines in Fig. 5). We will remark three points on the T dependence of ρ. First, it is a piece of evidence for strong correlation that ρ continues to decrease with decreasing T down to 4.2 K where no phonons are thermally excited. At least we can say that the conduction in this system is not dominated by the conventional electron-phonon scattering. Second, the T dependence of ρ of this system is not typical for strongly correlated systems. In usual strongly correlated systems, resistivity and electron-electron scattering are proportional to $(k_BT/E_F)^2$. Most of heavy fermions,[8] organic conductors,[9] transition-metal oxides[10,11] show $\rho\propto T^2$. As shown in the inset of Fig. 5, ρ for $Na_{1.1}Co_2O_4$ is not proportional to T^2 at any temperatures. A prime exception is the T-linear resistivity in high-T_c superconductors.[12] Actually, ρ and S of $NaCo_2O_4$ are qualitatively consistent with some theories for high-T_c superconductors.[13,14] In particular, ρ of $Na_{1.1-x}Ca_xCo_2O_4$ can be explained by adjusting the parameters in Ref. 13. Thirdly all the samples show no indication of localization. This means that the mean free path (MFP) of the carriers is much longer than the lattice parameters,[2] and that the carriers do not feel the disorder in the Na layer. On the other hand, phonons will be affected by the disorder in the Na layer, since the disorderd Na^+ ions make ionic bonding with adjacent O^{2-} ions. In fact, a preliminary measurement has revealed that κ for $Na_{1.1}Co_2O_4$ is as low as 10 mW/cmK,[15] suggesting that MFP of the phonons is of the order of the lattice spacing. Thus, MFP of the carriers is much longer than MFP of the phonons in $NaCo_2O_4$. We therefore propose that this material is a new class of ‘‘electron crystals and phonon glasses.’’[16]

Finally, let us comment on the strong correlation. Since the diffusive part of S corresponds to the transport entropy, as mentioned above, larger electronic specific heat can give larger S. Thus S would be enhanced if the carriers could couple with some outside entropy such as optical phonon, spin fluctuation, or orbital fluctuation. Recently a similar scenario is independently proposed by Palsson and Kotliar.[18] Heavy fermions or valence-fluctuation systems are indeed the case, some of which show large S.[1] Very recently Ando *et al.*[17] have measured the specific heat of $Na_{1.1-x}Ca_xCo_2O_4$ at low temperatures, and have found a large electronic specific heat of 48 mJ/mol K^2, which is one order of magnitude larger than conventional metals.

In summary, we have prepared polycrystals of $Na_{1+x}Co_2O_4$ and $Na_{1.1-x}Ca_xCo_2O_4$, and measured the resistivity and thermopower from 4.2 to 300 K. The excess Na and the substituted Ca affect the transport properties of $NaCo_2O_4$ differently. The former seems to decrease the effective conducting region, and the latter decreases the carrier density. The temperature dependence of the resistivity is drastically changed by substituting Ca, which strongly suggests that the scattering mechanism depends on the carrier density. Combining this with the peculiar temperature dependence of the resistivity, we conclude that strong electron-electron correlation plays an important role in this compound.

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*Author to whom correspondence should be addressed. Electronic address: terra@mn.waseda.ac.jp

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