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Large thermoelectric power in $NaCo_2O_4$ single crystals

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We measured and analyzed the transport properties of single-crystal $NaCo_2O_4$, which is a metallic transition-metal oxide consisting of a two-dimensional triangle lattice of Co. Reflecting the crystal structure, the resistivity is highly anisotropic between in- and out-of-plane directions, and the in-plane resistivity is as low as 200 $\mu\Omega$ cm at 300 K. Most strikingly, the in-plane thermoelectric power of $NaCo_2O_4$ is about 100 μV/K at 300 K, which is nearly ten times larger than that of typical metals. The large thermoelectric power and the low resistivity suggest that $NaCo_2O_4$ is a potential thermoelectric material. [S0163-1829(97)52144-8]

The discovery of high-temperature superconductors (HTSC's) (Ref. 1) encouraged scientists to hunt for unknown materials that are scientifically interesting and/or technologically important. In fact, new materials and new phenomena were discovered one after another in the past decade.[2] We have been investigating a new material as a reference for HTSC's, and have paid attention to $NaCo_2O_4$. $NaCo_2O_4$ belongs to a bronze-type compound expressed as A_xBO_2 ($0.5 \leqslant x \leqslant 1$), which was first identified by Jansen and Hoppe.[3] An important similarity to HTSC's is that $NaCo_2O_4$ is a layered transition-metal oxide as is schematically shown in Fig. 1(a), where Na (50% occupied) and CoO_2 are alternately stacked along the c axis. Thus the physical properties are expected to be highly two dimensional (2D). However, the CoO_2 layer is different in structure from the CuO_2 layer of HTSC's; the former is a 2D triangle lattice shown in Fig. 1(b), and the latter is a 2D square lattice. Recently Tanaka, Nakamura, and Iida[4] have shown that polycrystalline $NaCo_2O_4$ is a good metal down to 12 K, whereas it shows Curie-Weiss-like susceptibility instead of the Pauli paramagnetism. According to their results, $NaCo_2O_4$ can be regarded as a doped 2D triangle spin lattice, which is worth comparing with the CuO_2 layer.

We have studied the transport properties of single-crystal $NaCo_2O_4$, and have found, most unexpectedly, that it exhibits one order of magnitude larger thermoelectric power (100 μ/K at 300 K) than HTSC's, while it has as low resistivity (200 $\mu\Omega$cm at 300 K) as HTSC's. These parameters show that $NaCo_2O_4$ is a promising candidate for thermoelectric material.[5–7] Furthermore it has as low mobility as metals (13 cm^2/V s at 300 K), which is strikingly against the common sense that dirty conductors are not suitable for thermoelectric materials.[5] According to this result, thermoelectric materials can be discovered in the opposite direction of the previous guiding principle that good thermoelectric materials will be

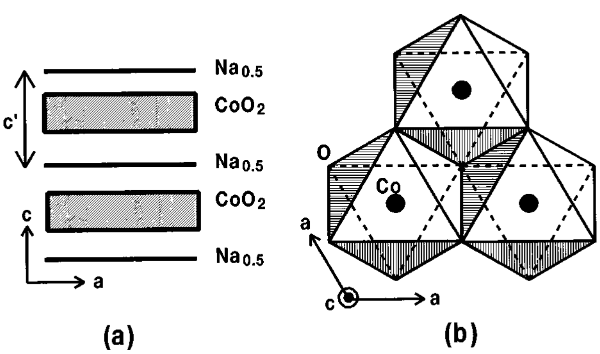

FIG. 1. A schematic picture of the crystal structure of $NaCo_2O_4$. (a) The layered structure; (b) the CoO_2 layer.

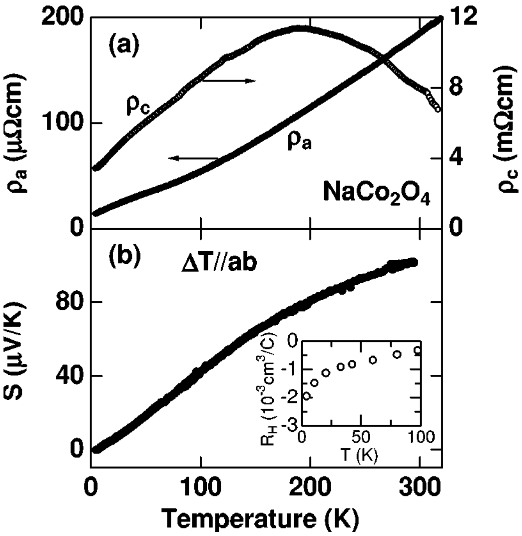

FIG. 2. (a) In-plane (ρ_a) and out-of-plane (ρ_c) resistivity of $NaCo_2O_4$ single crystals. (b) In-plane thermoelectric power (S) of $NaCo_2O_4$ single crystal. The inset shows the in-plane Hall coefficient (R_H) of $NaCo_2O_4$ single crystal.

found in narrow-gap semiconductors with high mobility.

Single crystals of $NaCo_2O_4$ were prepared by a NaCl-flux technique. A mixture of high-purity powders (Na_2CO_3:Co_3O_4:NaCl=1:1:5~6) was ground in an Al_2O_3 crucible, heated at 1050 °C for 5 h, and slowly cooled down to 850 °C by 2.5–5 °C/h. The grown crystals were then washed in water to remove the NaCl flux. The crystals were thin along the c axis with a typical dimension of 1.5×1.5 ×0.02 mm.[3]

Resistivity was measured with a dc current I of 1–5 mA in a four-probe configuration along the in-plane direction ($I \perp c$), and in a ring configuration along the out-of-plane direction ($I \| c$). Thermoelectric power was measured only along the in-plane direction, where one edge of the sample was pasted on a sapphire plate with the other pasted on a sheet heater. Temperature (T) was monitored by two diode thermometers attached on the edges. The contribution of copper leads was carefully subtracted.

Figure 2(a) shows the in-plane (ρ_a) and out-of-plane (ρ_c) resistivities of $NaCo_2O_4$ crystals. The resistivity is anisotropic in magnitude, and in the T dependence as well. The ratio of the resistivities ρ_c/ρ_a is around 200 at 4.2 K, which is comparable to the values for $La_{2-x}Sr_xCuO_4$ (Ref. 8) and Sr_2RuO_4 (Ref. 9). The electronic states can be thus regarded as quasi-2D, as was expected from the layered structure. The T dependence of ρ_a is consistent with Ref. 4, and the magnitude is as low as ρ_a of typical HTSC's. It should be emphasized that ρ_c shows a crossover near 200 K from metallic to semiconducting behavior with increasing T. This is similar to ρ_c of Sr_2RuO_4,[10] where the semiconducting ρ_c at high T is understood as incoherent hopping owing to $\ell_c \leq c'$ [ℓ_c is the c-axis mean free path, and c' is the interlayer spacing shown in Fig. 1(a)].

Figure 2(b) shows the in-plane thermoelectric power (S) of $NaCo_2O_4$. The magnitude of S is 100 μV/K at 300 K, which is about ten times larger than a typical S of metals and HTSC's.[11] Furthermore, the sign of S is opposite to the sign of the Hall coefficient shown in the inset of Fig. 2(b),[12] implying that S cannot be explained by a simple free-electron picture.[13] The large S accompanied by low ρ_a suggests that $NaCo_2O_4$ is applicable to thermoelectric devices.

A thermoelectric device is a device that converts heat into electric energy through the thermoelectric power of solids.[5] It also converts electric energy into heat through the Peltier effect.[14] Since there is no theoretical upper limit of $|S|$, it can be, in principle, as efficient as any other energy-conversion systems. In addition, the lifetime of the device can be as long as the lifetime of the material from which the device is made. More importantly, the device is environmentally friendly in the sense that it produces essentially no waste matter. For a thermoelectric application, large $|S|$ and low ρ are required. Usually $|S|$ and ρ are larger for smaller carrier density (n), and the output power takes a maximum at an optimal density n_0 ($\sim 10^{19}$ cm^{-3}), which corresponds to n for doped semiconductors.[5] In the fixed n_0, only the way to get low ρ is to find a material with high mobility (μ). Consequently semiconductors with n_0 and high μ (10^2-10^3 cm^2/V s) have been applied to thermoelectric devices.[5–7]

A significant feature in $NaCo_2O_4$ is that it has lower μ than doped semiconductors. Here we will show a rough estimate of μ at 300 K using the Boltzmann theory of metals and the effective-mass approximation, where n is T independent and $\mu \propto \ell \propto 1/\rho$. First let us evaluate the in-plane mean free path ℓ_a. As mentioned above, the maximum of ρ_c (12 mΩ cm) indicates $\ell_c \sim c' = 5.4$ Å, and we get $\ell_c \sim$ 16 Å at 4.2 K ($\rho_c \sim 4$ mΩ cm). Then using $\ell_a/\ell_c \sim v_a^F/v_c^F \sim \sqrt{\rho_c/\rho_a}$ (where v_i^F is the Fermi velocity along the i direction), we get $\ell_a \sim 16 \times \sqrt{200} \sim 230$ Å at 4.2 K. The next step is to obtain $k_a^F \ell_a$ from the equation of $k_a^F \ell_a = hc'/e^2\rho_a$, where k_a^F, h, and e is the in-plane Fermi wave number, the Planck constant, and unit charge, respectively. Note that we assume the 2D conduction along the a axis.[15] By substituting $\rho_a = 20$ $\mu\Omega$cm, we get $k_a^F \ell_a \sim 70$ at 4.2 K. Finally μ is calculated as $\mu \sim 2\pi e \ell_a / h k_a^F \sim 120$ cm^2/Vs at 4.2 K, and μ at 300 K is estimated to be 13 cm^2/V s ($\rho_a \sim 180$ $\mu\Omega$ cm). This result quantitatively agrees with measured Hall coefficient ($|R_H| \sim 2 \times 10^{-3}$ cm^3/C at 4.2 K). The obtained μ is much lower than μ of semiconductors, and in this context we regard $NaCo_2O_4$ as a dirty conductor.

TABLE I. Various physical parameters for $NaCo_2O_4$ and Bi_2Te_3 (Ref. 6) at 300 K. ρ, S, and μ are resistivity, thermoelectric power, and mobility, respectively. Note that ρ and S of $NaCo_2O_4$ are the in-plane data.

Parameters	Unit	$NaCo_2O_4$	Bi_2Te_3
ρ	mΩ cm	0.2	1
$\|S\|$	μV/K	100	200
S^2/ρ	μW/K^2 cm	50	40
μ	cm^2/V s	13	150

In Table I, various parameters of $NaCo_2O_4$ are compared with those of Bi_2Te_3,[6] a typical thermoelectric material. Although S is smaller in $NaCo_2O_4$ than in Bi_2Te_3, ρ is also lower to make the power factor (S^2/ρ) comparable. A remarkable difference is that μ is one order of magnitude lower in the former than in the latter, indicating that a dirty conductor can be as efficient as other thermoelectric materials. The low μ with the low ρ means that $NaCo_2O_4$ has much larger n than Bi_2Te_3, and that S is not simply determined by n. If so, S and ρ can be changed independently, which may break through the limitation derived from the conventional theories.

Finally we point out two future issues. (i) The origin of the large $|S|$ is an open question. A possible scenario is that S arises from spin fluctuation, as is similar to heavy fermions and/or valence-fluctuation systems.[17] The T dependence of ρ_a and S is, at least qualitatively, consistent with the theories of 2D metals with spin fluctuation by Moriya, Takahashi, and Ueda[18] and by Miyake and Narikiyo.[19] (ii) In addition to large $|S|$ and low ρ, low thermal conductivity (κ) is required for a real thermoelectric application.[20] We did not measure κ in the present study, and thus it should be further examined whether $NaCo_2O_4$ is really better for application. Actually a new thermoelectric material $IrSb_3$ shows larger S^2/ρ than Bi_2Te_3,[16] but shows less $S^2/\rho\kappa$ because of its high thermal conductivity.[7] In a preliminary study,[21] however, polycrystalline $NaCo_2O_4$ shows as low κ ($\sim$15 mW/cm K at 300 K) as Bi_2Te_3 and, hopefully, it will be qualified as a new thermoelectric material.

In summary, we prepared single crystals of metallic layered transition-metal oxide $NaCo_2O_4$, and measured the anisotropic resistivities and thermoelectric power. We have found that the in-plane thermoelectric power is unusually large (100 μV/K at 300 K), while the in-plane resistivity is quite low (200 $\mu\Omega$ cm at 300 K). These results indicate that $NaCo_2O_4$ is a potential thermoelectric material, whose power factor is comparable to a typical thermoelectric material such as Bi_2Te_3. Most importantly, $NaCo_2O_4$ has relatively low mobility (13 cm^2/Vs at 300 K), which is strikingly against the common sense that a low-mobility conductor cannot be a thermoelectric material. This implies that a new thermoelectric material may exist beyond the previous guiding principle.

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