

Physics in the hexagonal CoO_2 block in NaCo_2O_4

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Since large thermopower and low resistivity were found in single-crystal NaCo_2O_4 in 1997, the layered cobalt oxides have been extensively investigated as a promising candidate for a thermoelectric oxide. They have set us free from the “superstition” that oxides are unsuitable for thermoelectrics. Following NaCo_2O_4 , other related cobalt oxides have been found to show good thermoelectric performance, and all of which are the layered material consisting of the CdI_2 -type hexagonal CoO_2 block and the charge reservoir block. Obviously the CoO_2 block is a key ingredient for high thermoelectricity. Here we will discuss the basic physics underlying the layered Co oxides after a brief overview of their thermoelectric properties.

Key words: thermoelectric material, transition-metal oxide, strong correlation,

1. INTRODUCTION

A thermoelectric material can generate electric power through the Seebeck effect, and can pump heat through the Peltier effect [1]. Thus far, semiconductors of high mobility have been used as the thermoelectric materials, and oxide have been believed to be unsuitable because of poor mobility.

Since we discovered the large thermopower and the low resistivity in a NaCo_2O_4 single crystal in 1997 [2], we have proposed that some kinds of oxides can be a thermoelectric material [3,4]. Soon after our discovery, the high thermoelectric properties of NaCo_2O_4 were verified by other groups. Ohtaki et al. [5] found that the polycrystalline samples of NaCo_2O_4 show the dimensionless figure of merit ZT reaches 0.8 at 1000 K. Fujita et al. [6] have succeeded in measuring the thermal conductivity of a NaCo_2O_4 single crystal, and found that ZT exceeds unity at 800 K. These results strongly suggest that NaCo_2O_4 is a promising candidate for a thermoelectric oxide.

Following NaCo_2O_4 , $\text{Ca}_3\text{Co}_4\text{O}_9$ [7-9], $\text{Ca}_2(\text{Cu}, \text{Co})_2\text{Co}_2\text{O}_y$ [10], $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Co}_2\text{O}_y$ [11-13], $\text{TlSr}_2\text{Co}_2\text{O}_y$ [14], and $(\text{Pb}, \text{Co})\text{Sr}_2\text{Co}_2\text{O}_y$ [15] have been found to show good thermoelectric performance. They show large thermopower of 100-150 $\mu\text{V}/\text{K}$, low resistivity of 0.2-7 $\text{m}\Omega\text{cm}$. and low lattice thermal conductivity of 20-30 $\text{mW}/\text{cm K}$ at room temperature. These values are exceptionally superior to those of other oxides, and their ZT exceeds unity above 800 K. This means that their thermoelectric performance is comparable with that of the conventional thermoelectric materials such as PbTe and $\text{Si}_{1-x}\text{Ge}_x$.

Figure 1 shows the crystal structures of the layered cobalt oxides. They share a common unit of the CdI_2 -type hexagonal CoO_2 block, which reminds us of the CuO_2 plane in high- T_c superconductors (HTSC). Thus, just as the CuO_2 plane in HTSC, the hexagonal CoO_2 block should be a key ingredient for the unusually high thermoelectric performance of the layered Co

oxides. Very recently, Fujii and Terasaki [16] have proposed a block-layer concept for the layered Co oxides, as is established in the material design for HTSC.

2. ORIGIN OF LARGE THERMOPOWER

The thermoelectric power is a good probe for the heat flow of a carrier in solids. Electric current density \mathbf{j} and thermal current density \mathbf{q} are coupled by electric field (∇V) and temperature gradient ($-\nabla T$) as,

$$\mathbf{j} = \sigma \nabla V + \alpha S (-\nabla T)$$

$$\mathbf{q} = \sigma S T \nabla V + \kappa (-\nabla T)$$

where σ , S , and κ are the electric conductivity, the thermoelectric power and the thermal conductivity, respectively. Then in the absence of the temperature gradient ($\nabla T=0$), the above equations reduce to

$$\mathbf{q}/T = S \mathbf{j}$$

Since \mathbf{q}/T is the entropy current density, the thermoelectric power S is the ratio of the entropy to the charge per carrier. This is directly seen in the Heikes formula, a simple (but rigorous) asymptotic form of the thermoelectric power in a high temperature limit where the thermal energy $k_B T$ is much larger than the transfer energy (bandwidth).

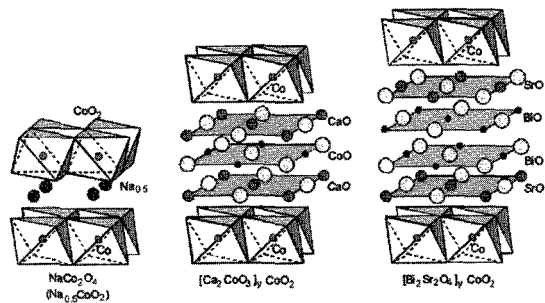


Fig. 1 Crystal structures of the layered cobalt oxides.

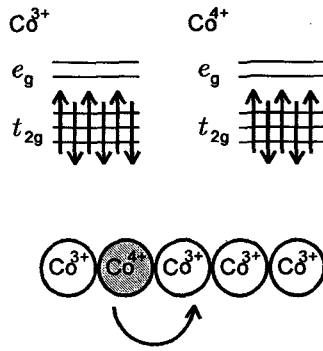


Fig.2 Electron configurations of Co^{3+} and Co^{4+} in the layered cobalt oxides (upper figure), and schematic picture of electric conduction (lower figure)

Koshibae et al. [17] proposed an extended Heikes formula written as

$$S = \frac{k_B}{C} \log \frac{g_A - p}{g_B (1-p)}$$

where g_A and g_B are the degeneracy of the electron configuration of A and B ions, C is the charge difference between A and B ions, and p is the atomic content of the A ion. Note that

$$k_B \log \frac{g_A - p}{g_B (1-p)}$$

is equal to the entropy per carrier, and S for $p=0.5$ is simply reduced to $k_B(\log g_A/g_B)/C$.

Let us apply the above formula to NaCo_2O_4 . Magnetic measurements reveal that the Co^{4+} and Co^{3+} ions are in the low spin state in NaCo_2O_4 . As shown in the upper part of Fig. 2, the configuration of the low-spin-state Co^{3+} is $(t_{2g})^6$, whose entropy is zero. On the other hand, the low-spin-state Co^{4+} has a hole in the t_{2g} states, which is six-fold degenerate (two from spin and three from t_{2g} orbitals) to carry large entropy of $k_B \log 6$. Suppose electric conduction occurs by exchanging Co^{3+} and Co^{4+} , as is shown in the lower part of Fig. 2. Then a hole on Co^{4+} can carry a charge of $+e$ with entropy of $k_B \log 6$, which causes a large thermopower of $k_B \log 6/e$ ($\sim 150 \mu\text{V/K}$). This is very close to the saturated values of the thermopower of the layered cobalt oxide shown in Fig. 3. Note that carriers in degenerate semiconductors have no internal degrees of freedom: they can only carry entropy due to their kinetic energy. In this sense, a hole in NaCo_2O_4 can carry much larger entropy than degenerate semiconductors, which leads us a new design for thermoelectric materials.

Although Koshibae's theory has successfully explained the high-temperature limit thermopower of NaCo_2O_4 , the problem is not so simple. The thermopower of NaCo_2O_4 is $100 \mu\text{V/K}$ at 300 K, which is about $2/3$ of $k_B \log 6$, which means that the large amount of entropy of $k_B \log 6$ in the high-temperature limit ($\sim 10^4$ K) survives down to 10^2 K.

We think it important that NaCo_2O_4 shows no structural, electric, and magnetic transitions from 2 to 1000 K. Usually various phase transitions occur in order to release an excess entropy per sites in the strongly correlated systems. Then, if all the phase transition were

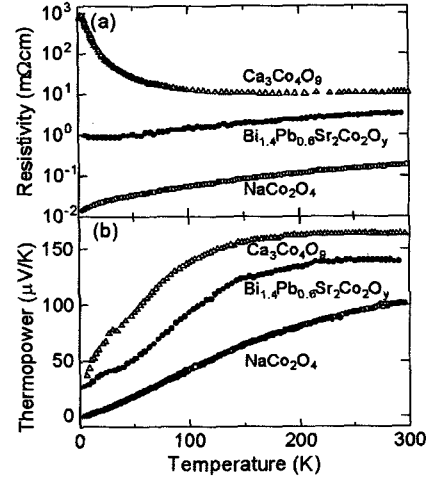


Fig. 3 Thermoelectric properties of single crystals of various layered cobalt oxides. Note that the data are taken along the CoO_2 layer.

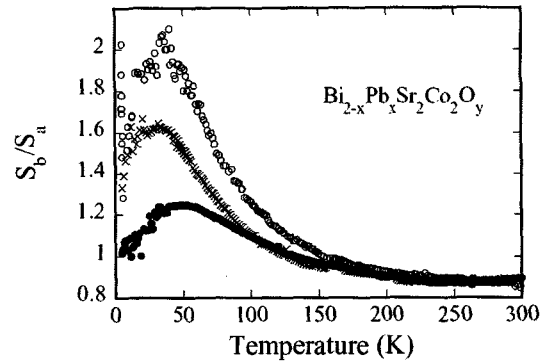


Fig. 4 In-plane anisotropy of the thermopower in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Co}_2\text{O}_y$. ($x=0$ (\bullet), $x=0.4$ (\circ) and $x=0.6$ (\times))

blocked, the large entropy would inevitably point to the conducting carriers to form a "heavy-fermion"-like electron.

In fact, the electron specific heat coefficient and the spin susceptibility for NaCo_2O_4 are just close to those for the valence-fluctuation compound CePd_3 , which has nearly the same values of S ($80 \mu\text{V/K}$ at 300 K) and ρ ($150 \mu\Omega\text{cm}$ at 300 K) [3]. Recently Valla et al. [18] have performed a photoemission experiment for the layered cobalt oxides, and have successfully observed the coherent state at low temperatures.

Another similarity to the heavy fermion is seen in the pressure effects. We have found large in-plane anisotropy in the hexagonal CoO_2 block of the misfit compounds [19]. This is unusual situation, because the hexagonal CoO_2 block itself should be isotropic on the basis of the point-group theory. We have attributed the in-plane anisotropy to the anisotropic pressure (or stress) arising from the misfit interface of the hexagonal CoO_2 block and the rock-salt square $\text{Bi}_2\text{Sr}_2\text{O}_4$ block. As shown in Fig. 4, the anisotropy of the thermopower reaches two for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Co}_2\text{O}_y$, which is anomalously large. As

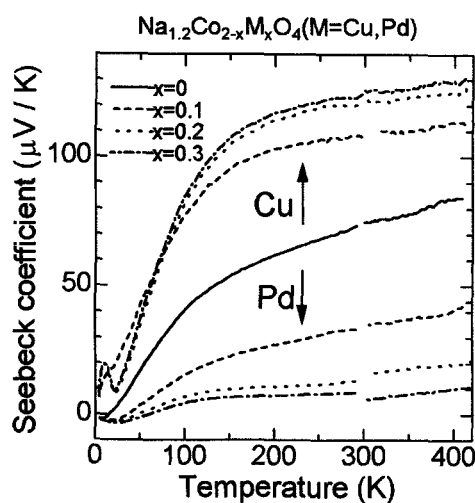
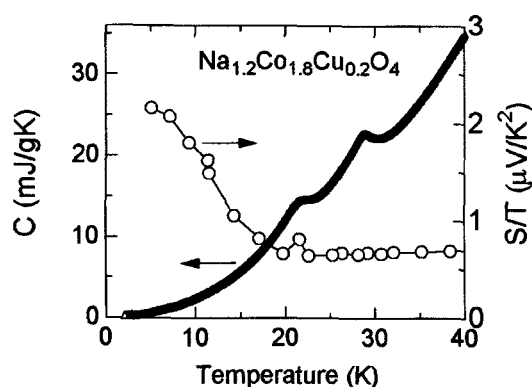


Fig. 5 Co-site substitution effects on the thermopower.

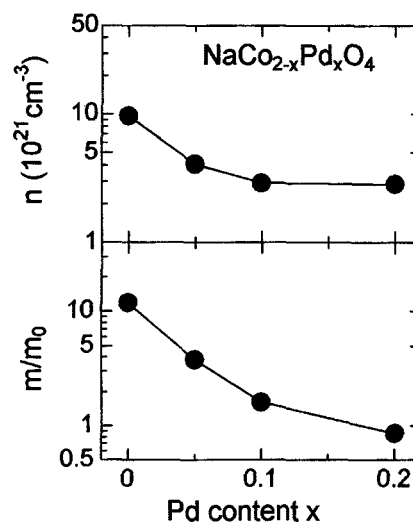

 Fig. 6 Phase transition observed in the specific heat and thermopower in Cu-substituted NaCo_2O_4 (see text).

is well known, the thermopower of heavy-fermion compounds are very sensitive to the pressure, where the thermopower changes by a factor of three upon less than 1-% lattice contraction [20].

3. IMPURITY EFFECTS

If it were essential that any phase transitions are suppressed in NaCo_2O_4 , some transition would occur against various perturbations. NaCo_2O_4 is a layered oxide consisting of a CoO_2 block and a Na layer. The electric conduction is highly two-dimensional, and the resistivity anisotropy is 100-200 between the intra- and inter-layer directions. Thus a small amount of substitution is expected to deteriorate the electric conduction. (Note that, according to the localization theory, a two-dimensional metal will be insulating at zero temperature in the presence of a finite amount of disorder). Contrary to this, the thermoelectric properties are improved against some kinds of impurities such as Cu and Pd.

Figure 5 shows Cu and Pd substitution effects on the thermopower in NaCo_2O_4 . With increasing Cu content, the thermopower enhances for all the temperature range. In addition, it shows a peak at 10 K (more precisely, a


 Fig. 7 Carrier concentration n and effective mass m plotted as a function of substituted Pd.

dip at 22 K) for the $x=0.2$ and 0.3 . This is a strong piece of evidence that the phase transition occurs at low temperatures. In contrast, the Pd substitution decreases the thermopower.

Figure 6 shows specific heat and the T -linear coefficient of the thermopower S/T as a function of temperature. Since S/T is inversely proportional to the carrier concentration (the density of states), Figure 6 indicates that (pseudo)gap is opened below 22 K. The jump in specific heat near 22 K directly evidences the phase transition. (The jump at 30 K is due to the impurity of Co_3O_4). We proposed that the 22-K transition is very similar to the spin-density-wave (SDW) in Cr [21].

The Cu substitution enhances the instability, and eventually causes the SDW-like transition at 22 K. This type of transition is called "order from disorder". In other words, instabilities against various phases are competing or disordering in NaCo_2O_4 , and any phase transitions are prohibited down to low temperatures. This does not mean that NaCo_2O_4 is far from the instability of phase transitions, but rather, is very susceptible to various transitions against various perturbations. $\text{Na}_{1.5}\text{Co}_2\text{O}_4$ exhibits a ferromagnetic transition at 22 K [22], possibly owing to the structure instability of the γ phase. Very recently, μSR measurement has revealed that the 22-K transition in $\text{Na}_{1.5}\text{Co}_2\text{O}_4$ is an SDW-like static magnetic order [23]. We also note that $(\text{Bi,Pb})_2\text{Sr}_2\text{Co}_2\text{O}_y$ shows a ferromagnetic transition at 4 K [24] due to the lattice misfit.

Figure 7 shows the Pd substitution effects on the carrier concentration and the effective mass [25]. With increasing Pd content, these two quantities rapidly decrease. In particular, the effective mass decreases by one order of magnitude from 0 to 0.2, which is a predominant origin of the decrease of thermopower shown in Fig. 5. This strongly suggests that the effective mass of NaCo_2O_4 is basically determined by the strong correlation, not the curvature of the band dispersion, because the calculated band has no singular curvature

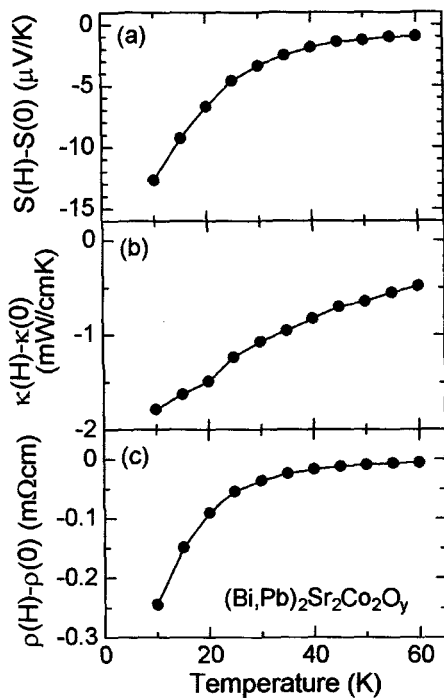


Fig. 8 Change in the thermoelectric parameters of $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Co}_2\text{O}_y$ single crystals induced by an applied field of 7 T.

near Fermi level. Thus the Pd effects are another piece of evidence for the unusual electronic states of the layered cobalt oxides.

4. MAGNETO-THERMOELECTRIC EFFECTS

Magneto-transport is a powerful probe for the spin-charge coupling. A prime example is seen in the colossal magneto-resistive (CMR) materials, where magnetic field induces a metal-insulator transition. Very recently Wang et al. [26] have found that the thermopower of Na_xCoO_2 is highly dependent on magnetic field. A similar result is independently observed in Bi-Ca-Co-O single crystals by Maignan et al. [27]. However, the magnetic field modifies not only the thermopower, but also the resistivity and the thermal conductivity. Thus the field dependence of the three parameters should be analyzed consistently [28].

Figure 8 shows the magnetic-field dependence of the thermoelectric parameters. The applied field decreases the resistivity, thermopower, and thermal conductivity, although their field dependences are different. We should note that the magneto-thermal conductivity (not the magneto-thermal resistivity) is negative, whereas the magnetoresistance is negative. In other words, magnetic field increases the electric current, and decreases the thermal current. Since the thermal conductivity is mainly due to phonons, the magneto-thermal conductivity should also be attributed to phonons.

As is similar to the Cu-substituted NaCo_2O_4 , $(\text{Bi}, \text{Pb})_2\text{Sr}_2\text{Co}_2\text{O}_y$ opens the SDW-like pseudogap below about 50 K, and SDW is suppressed by the applied field. Thus, the observed magneto-transport in this system can be analyzed in terms of the pseudogap suppression by

external field. In fact, the observed thermo-magnetic effects are remarkable below about 60 K, close to the pseudogap temperature.

Thermopower of the layered cobalt oxides is inversely proportional to the carrier concentration (the density of states), and the negative magneto-thermopower implies that the magnetic field suppresses the pseudogap. The suppressed pseudogap would increase conduction electrons that scatter phonons through the electron-phonon interaction. This would shorten the phonon mean free path to give negative magneto-thermal conductivity.

The interpretation of magnetoresistance is more complicated. The external field increases the carrier concentration, but also modifies the scattering time through the electron-electron (or magnetic) scattering. In fact the magnetoresistance is either negative or positive in the NaCo_2O_4 family. Usually the magnetoresistance of NaCo_2O_4 is negative at low temperatures [3,4], but the Pd-substituted samples show a large positive magnetoresistance [25]. Rapidly-quenched Na_xCoO_2 samples also show a large positive magnetoresistance that obeys Kohlar's law [22]. These results imply that the change in the density of states and the change in the scattering time are competing with the same weight.

5. SUMMARY

In this article, we have reviewed the physics occurring in the hexagonal CoO_2 block, mainly focusing on the low-lying excitations such as transport and thermodynamic properties. The layered cobalt oxides do not only show high thermoelectric performance, but also exhibits interesting features from the viewpoint of basic science.

Carriers in oxides are often coupled with the optical phonons, the spin degrees of freedom and the orbital degrees of freedom. These couplings form exotic electronic states such as polarons, heavy fermions, and spin liquids. Furthermore, the geometry and the dimensionality are easy to change in certain classes of oxides, where layered structures, ladder structures, chain structures can be controlled. Therefore I believe that many functional materials including thermoelectric materials will still sleep unknown. I hope that NaCo_2O_4 is just the beginning, and that a thermoelectric oxide of higher performance will appear in near future.

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