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Magnetic Field Effects on Thermoelectric Properties of $[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ Single Crystals

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The large thermopower seen in the layered cobalt oxides is attributed to large entropy, which comes from the spin and orbital degrees of freedom. It is also important to maintain the large entropy down to low temperature keeping away from phase transitions. Here we have measured the field dependence of the resistivity, thermopower and thermal conductivity of the layered cobalt oxide $[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ single crystals to investigate the relations between the phase transitions and the thermoelectric properties. The magnetic field reduces the resistivity, thermopower and thermal conductivity below about 60 K. This is considered to be due to the suppression of the spin-density-wave-like phase fluctuation.
Key words: layered cobalt oxide, spin density wave, magnetic field effect, strong electron-electron correlation

1. INTRODUCTION

The layered cobalt oxides having a CdI_2-type hexagonal CoO_2 layer exhibit a good thermoelectric performance especially at high temperatures [1-4]. This is attributed to the strong electron-electron correlation, where the spin and orbital degrees of freedom provide large entropy of $k_B$log6 [5,6]. It is also important that the large entropy at high temperature cannot be released through phase transitions down to sufficiently low temperature. Thus, the instabilities against various phases may play an important role to maintain the large thermopower [7].

Recently, various experiments have reported that some layered cobalt oxides show the spin-density-wave (SDW) like behavior at the low temperature. Terasaki et al. found a clear specific heat jump in copper substituted $NaCo_2O_4$ around 22 K, and assigned to the SDW-like transition [8]. Similar phase transition was observed in the sodium-rich compound $Na_{0.75}CoO_2$ [9]. Sugiyama et al. have studied muon spin rotation–relaxation spectroscopy and found that the various cobalt oxides, such as Sr, Y, or Bi substituted $Ca_3Co_4O_9$, exhibit SDW-like magnetic structure [10,11]. Thus, the SDW-like magnetic structure is considered to be generic to the layered cobalt oxides.

$[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ is also considered to be this kind of system [12]. Then, in order to investigate the relations between phase transitions and thermoelectric properties, we have measured the field dependence of the resistivity, thermopower and thermal conductivity of the layered cobalt oxide $[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ single crystals. The magnetic field suppresses the SDW-like fluctuation to recover the density of states and reduce the resistivity, thermopower [13,14] and thermal conductivity. In this paper, we will discuss the magnetic field effect on the thermoelectric properties, focusing on the suppression of the SDW-like fluctuation. And we will discuss the relation between the phase transitions and the thermopower.

2. EXPERIMENTAL

Single crystals of $[Bi_{1.6}Pb_{0.4}Sr_2O_4]_yCoO_2$ were grown by a traveling solvent floating zone method. Detailed growth condition and the characterization of the crystals were published elsewhere [12]. Large single crystals with the size of $5\times5\times0.1mm^3$ enable us to measure the electrical and thermal transport precisely.

The resistivity and Hall coefficient were measured by standard six-probe method with an AC resistance bridge. The thermopower was measured by steady-state method. The sample was bridged across the two copper blocks acting as heat baths. One of the copper block was thermally anchored to the heat sink and the small heater was attached to the other copper block. The temperature difference ΔT across the sample was measured with two cernox thermometers attached on the two copper blocks. The magnetic field was applied by using closed-cycle refrigerator in a room-temperature bore of the liquid-helium-free superconducting magnet. The electric and thermal currents were applied along ab-plane and the magnetic field was applied along c-axis (perpendicular to the electric and thermal current) sweeping from -7T to 7T.

Figure 1(a), (b) show heater current dependence of temperature difference ΔT and sample voltage ΔV at 10 K respectively. As seen in this figure, ΔT and ΔV are proportional to the square of the heater current

indicating that the temperature rise caused by Joule-heat was precisely measured. In the inset of Figure 1(a), (b), the relative change of the temperature difference $\Delta T(H)-\Delta T(0)$ and sample voltage $\Delta V(H)-\Delta V(0)$ are potted against magnetic field. At 10 K, ΔV decreases with increasing magnetic field, while ΔT increase with increasing magnetic field. This indicates that the thermopower and the thermal conductivity decrease with increasing magnetic field. On the other hand, ΔT and ΔV at 65 K do not change with magnetic field.

The thermal conductivity calculated from ΔT was overestimated (abut 400 mW/cmK), because all the thermal current, which was supplied from the heater, did not run across the sample. However, we can estimate the field dependence of the thermal conductivity $([\kappa_H-\kappa_0]/\kappa_0)$ from the temperature difference.

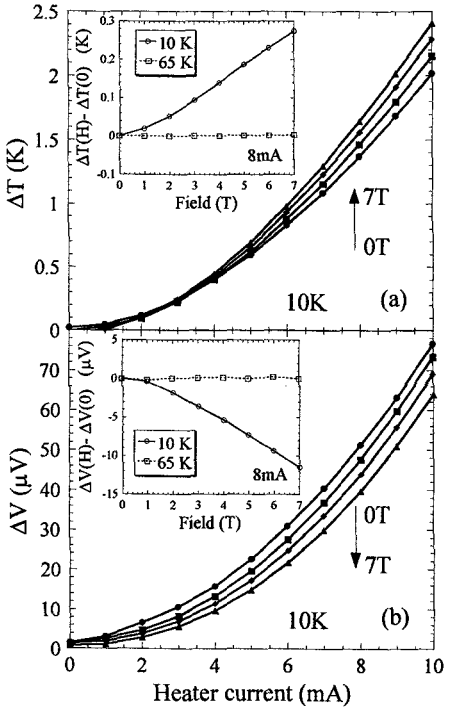

Figure 1: Heater current dependence of the temperature difference ΔT (a) and sample voltage ΔV (b) at 10 K. Inset: Field dependence of temperature difference $\Delta T(H)-\Delta T(0)$ and sample voltage $\Delta V(H)-\Delta V(0)$ with the heater current of 8 mA.

3. RESULTS and DISCUSSION

Figure 2(a) shows temperature dependence of the resistivity ρ and Hall coefficient R_H of $[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ single crystals[15]. The resistivity shows metallic behavior down to about 60 K. Similar temperature dependence is observed in the Hall coefficient, which indicate that the mobility $\mu=R_H/\rho$ is nearly independent of temperature. As seen in Fig. 2(a), the resistivity and the Hall coefficient increase with decreasing temperature below about 60 K. Figure 2(b) shows temperature dependence of the thermopower S and S/T. The thermopower is 150 μV/K at room temperature, and decrease with decreasing temperature. Similarly to the Hall coefficient, S/T increase at low temperature. The diffusive part of the thermopower in a quasi two-dimensional system is written as

$$S = \frac{\pi k_B^2}{2e\hbar^2 d}\frac{m^*}{n}T$$

where m^* and d are the effective mass and the c-axis length respectively[16]. As pointed out by Ito and Terasaki [17], if we assume that the thermopower of $[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ is essentially proportional to temperature (if the coefficient depend on temperature), S/T is proportional to m^*/n. These results suggest that the carrier density (or density of states) decreases by opening of pseudogap at low temperature. We consider the origin of the pseudogap as a fluctuation of SDW.

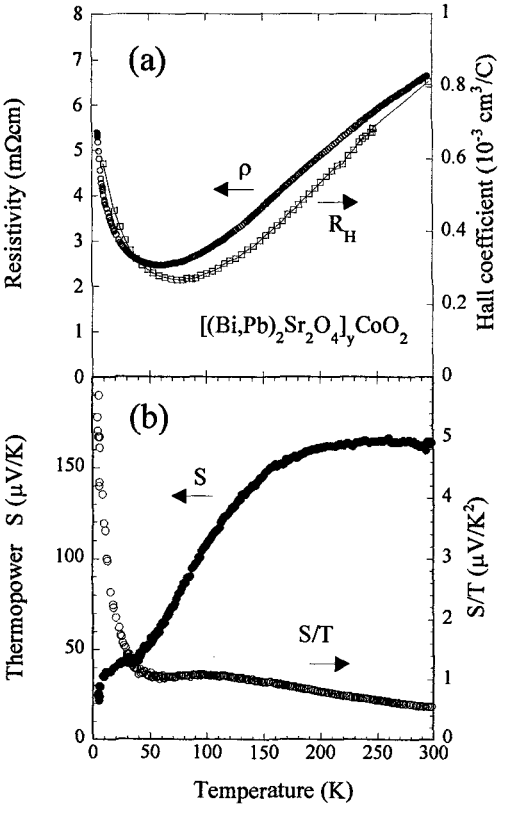

Figure 2: (a) Temperature dependence of resistivity and Hall coefficient. (b) Temperature dependence of the thermopower S and S/T.

Figure 3 shows magnetic field dependence of (a) resistivity $[\rho(H)-\rho(0)]/\rho(0)$, (b) thermopower $[S(H)-S(0)]/S(0)$, and (c) thermal conductivity $[\kappa(H)-\kappa(0)]/\kappa(0)$. The applied field suppresses the resistivity, thermopower, and thermal conductivity, and the negative field dependence disappear above around 60 K, which is almost coincide with the upturn temperature of the

resistivity and Hall coefficient. The suppression of the resistivity and thermopower with magnetic field are considered to be due to the increase of the carrier density (density of state), which is caused by the suppression of the pseudogap. Note that the field dependence of the thermal conductivity is also negative, although the magneto-resistance is negative.

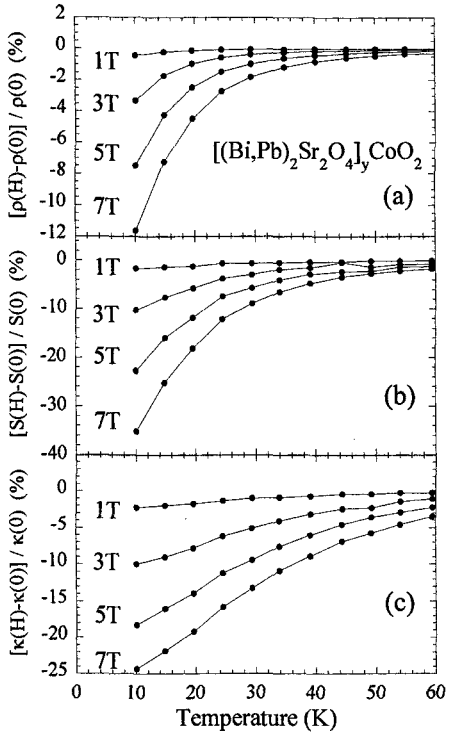

Figure 3: magnetic field dependence of (a) resistivity $[\rho(H)-\rho(0)]/\rho(0)$, (b) thermopower $[S(H)-S(0)]/S(0)$, and (c) thermal conductivity $[\kappa(H)-\kappa(0)]/\kappa(0)$.

According to the Wiedemann-Franz law, the ratio of the electric current and the thermal current is universal, because each electron carries the electric charge of e and the thermal energy of k_BT. Then, the relative change of the thermal conductivity with magnetic field is considered to be due to lattice contribution. Actually, the electron contribution estimated from the Wiedemann-Franz law is about 1mW/cm, which is about 3 % of the total thermal conductivity.

Terasaki pointed out that the thermal conductivity is larger than a conventional point-defect scattering theory below about 100 K [18]. This suggests that the phonon mean free path is enhanced by opening of the pseudogap. That is, the phonons are mainly scattered by conduction electrons through the electron-phonon scattering, and become long-lived when the carrier density is decreased (or the Fermi surface is partially gapped). Then, the thermal conductivity decreases with magnetic field due to the suppression of the pseudogap.

Similar suppression of the thermal conductivity is reported in the spin-Peierls compound $CuGeO_3$ [19]. Below the spin-Peierls transition temperature, it has a spin gap between the singlet and the lowest excited triplet states. When the spin-Peierls order disappears (the spin gap disappears) with applying magnetic field, the thermal conductivity decreases due to the scattering of the phonons by spin excitations.

Thus, the field dependence of the thermoelectric parameters is consistently understood by considering the pseudogap opened at low temperature. Although a jump in the specific heat is not observed in $[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ [15], SDW-like phase fluctuation (not a phase transition) may occur to reduce the density of states. We believe that the SDW-like phase is generic to the layered cobalt oxides.

Finally, we will briefly discuss the relation between the phase transitions and the thermopower. As is mentioned in introduction, the phase transitions are harmful to realizing good thermoelectric properties because the large entropy of the strong electron-electron correlation system would be released. Since cobalt oxide having a large thermopower consists of triangular lattice, frustration between spins suppresses the phase transition. Then, cobalt oxides are considered to be very close to the instability for various phase transitions, but never induce. A small amount of impurity, such as copper substitution or misfit structure, can induce the phase transition. On the other hand, a square lattice perovskite compounds give rise to various transitions. However, if we can suppress the phase transition, the thermopower should become large. For example, Mn oxide is expected to show large negative thermopower of -79 μV/K at high temperature [5]. The orbital-charge-spin ordering of $Ln_{0.5}Ba_{0.5}MnO_3$ (Ln = rare earth) with ordered Ln/Ba cations occurs relatively high temperature (about 300 K ~ 500 K), while Ln/Ba disordered compounds suppress the respective long-range orders, and the ordering temperature decrease (about 50 K ~ 300 K) [20]. Thus, in the case of square lattice perovskite, disorder suppresses the phase transition. Such system would improve the thermoelectric properties.

4. SUMMARY

We have investigated the spin-density-wave-like states in the $[(Bi,Pb)_2Sr_2O_4]_yCoO_2$ through measuring the field dependence of the resistivity, thermopower, and thermal conductivity. These parameters decrease with magnetic field, which is consistently understood by considering the suppression of the pseudogap. We consider that the spin-density-wave-like magnetic structure is generic feature for the layered cobalt oxides and that the prevention against phase transitions gives rise to high thermoelectric performance.

Lastly, we would like to propose the material design of strongly correlated system to achieve

good thermoelectric performance. First, the materials should have large entropy (large spin and/or orbital degree of freedom) at high-temperature. Second, the system should not exhibit phase transitions as cobalt oxide having a triangular lattice. Even if the system likely to give rise to phase transitions, such as square lattice perovskite, the suppression of the phase transition by random potential would improve thermoelectric performance.

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