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Electronic structure and thermoelectric power of layered cobalt oxides

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Introduction

Recently, layered cobalt oxides, $Ca_3Co_4O_9$, $Bi_2Sr_3Co_2O_9$, and $Na_{0.6}CoO_2$, attract interests as the most promising thermoelectric materials because these cobalt oxides possess high thermoelectric power and relatively low electrical resistivity though thermoelectric power, in general, decreases with decreasing electrical resisitivity. The figure of merit defined by $ZT = S^2T / (\kappa \cdot \rho)$ for these cobalt oxides, then, reaches nearly unity, that is comparable to or even higher than the value achieved in the commercial thermoelectric materilas. Here S, κ and ρ represent Seebeck coefficient, thermal conductivity, and electrical resistivity, respectively,

In this study, we performed resonant photoemission spectroscopy (RPES), soft x-ray emission spectroscopy (SXES), soft x-ray absorption spectroscopy (SXAS), and high-resolution ($\Delta E \leq 15$ meV) ultraviolet photoemission spectroscopy (HRUPS) on these three layered cobalt oxide to investigate the electronic structure that cause simultaneous possession of large thermoelectric power and low electrical resistivity.

Experimental Results

A narrow band of 1.5 eV in width was observed as an intense peak in photoemission spectra with its center at 1.0 eV below the Fermi level (E_F) for all cobaltites. This peak turns out to be less significant when Co 2*p*-3*d* resonance takes place, indicating that it consists mainly of O 2*p* and of small amount of Co 3*d* component. Less obvious hump-like structure observed at 1.0 eV below E_F in the Co $L\alpha_{1,2}$ SXES spectra lends a great support to this assignment.

It is of great importance to note here that E_F is located at the high-energy edge of this narrow band, and that the density of states at E_F ($N(E_F)$) stays negligibly small. We observed very small but finite Fermi edge in the high-resolution UPS spectra at room temperature, that is qualitatively consistent with their metallic electrical conductivity.

With decreasing temperature, only $Ca_3Co_4O_9$ shows gradual disappearance of the Fermi edge below 100K, while two other cobalt oxides keep to possess a distinct Fermi edge. Since electrical resistivity in $Ca_3Co_4O_9$ is reported to diverge below 100K[1], the opening of the energy gap across the Fermi level must be responsible for this divergence in the electrical resistivity.

Note here that the width of the energy gap has a strong temperature dependence. The temperature dependence of electrical resisitivity in $Ca_3Co_4O_9$, therefore, can not be analyzed with the ordinary method adopted for the thermal excitation-type conduction, the variable range hopping conduction, nor polaron hopping conduction. The presence of spin density wave below 100K is reported to exist in $Ca_3Co_4O_9$,[2] and it most likely cause the energy gap across the Fermi level.

The thermoelectric power were calculated from the measured UPS spectrum. We intentionally used spectra measured at high temperature rather than using that in low temperature, because information about the unoccupied band at energies up to $2k_BT$ from the Fermi level can be extracted by dividing the measured spectra with Fermi-Dirac distribution function. This method is only valid if the energy resolution of the measurement is much smaller than $4k_BT$ at the employed temperature.

Seebeck coefficient with metallic electronic conduction can be evaluated with the following equation.

$$S = \frac{1}{eT} \frac{\int N(\varepsilon)(\varepsilon - \mu)\frac{\partial f(\varepsilon)}{\partial \varepsilon} d\varepsilon}{\int N(\varepsilon)\frac{\partial f(\varepsilon)}{\partial \varepsilon} d\varepsilon} \qquad (1)$$

By using this equation and density of states below and above E_F deduced from the high resolution UPS measurements, we calculated absolute value and temperature dependence of the Seebeck coefficient. It is found that the calculated values show fairly good agreement with the measured ones not only in the absolute value but also in the temperature dependence. Thus we conclude that the steep slope in the density of states below E_F coupled with the negligibly small $N(E_F)$ must be attributed to the large thermoelectric power up to 200 μV/K observed for these cobalt oxides.

References

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