Spin-State Control: A Lesson from the Thermoelectric Cobalt Oxides

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The spin state is a fundamental concept in transition-metal complexes and compounds. The Coulomb potential given by the anions surrounding a transition-metal cation in complexes or solids lifts the degeneracy of the d orbitals on the cation. In particular, octahedrally coordinated anions split the five-fold energy levels into the two-fold degenerate e_g states and the three-fold degenerate t_{2g} states, and the energy gap between them often competes with the Hund coupling working between the d electrons on the same ion. When the e_g–t_{2g} gap is dominant, the d electrons occupy the lower t_{2g} level first. In contrast, when Hund's rule is dominant, the d electrons occupy the two levels in order to maximize the total spin number. The former is called the low spin state, and the latter is called the high spin state. The spin states of Co^{3+} ions are particularly important in the sense that the low spin state of $(t_{2g})^6$ is almost degenerate with the high spin state of $(e_g)^2(t_{2g})^4$. The perovskite cobalt oxide $LaCoO_3$ is a prime example, where the spin state gradually changes from the low to high spin state with increasing temperature. Concomitantly the cobalt oxides exhibit unconventional charge transport driven by the spin state crossover.

The spin-state related transport has received a considerable interest since the discovery of the good thermoelectric properties in the layered cobalt oxide Na_xCoO_2 [1]. This particular oxide shows thermoelectric conversion efficiency as good as the state-of-the-art thermoelectric materials (Fig. 1), although the carrier concentration is in the metallic density (10^{21}-10^{22} cm^{-3}). Based on a simple semiconductor physics, the thermopower is expected to be as small as 10^{-6} V/K at room temperature for such a metallic density. Koshibae et al. [2] proposed that additional entropy coming from the spin state plays an important role in the thermopower of the cobalt oxides.

After a brief introduction to the thermoelectric cobalt oxides, we show in this talk why and how the spin states affect the transport and magnetic properties in various cobalt oxides, by introducing two examples from our recent activities. The first one is the A-site ordered perovskite $Sr_3YCo_4O_{10.5}$ [3]. This material is a room temperature (weak)ferromagnet with a transition temperature of 370 K. Nakao et al. [4] have revealed that this transition is a spin-state ordering of the high-spin and intermediate-spin states (Fig. 2). We have found that the thermopower of this oxide is enhanced by external pressure, which is explained in terms of the pressure-induced spin state crossover. The second example is $LaRh_{1-x}Co_xO_3$, a solid solution of $LaCoO_3$ and $LaRhO_3$. Asai et al. have found a weak ferromagnetic order below 15 K for x=0.15. We should emphasize that a solid solution of the two nonmagnetic materials can be a ferromagnet.

References
[1] I. Terasaki et al.. Phys. Rev. B56 (1997) R12685.
[2] W. Koshibae. et al., Phys. Rev. B62 (2000) 6869.
[3] W. Kobayashi et al. Phys. Rev. B72 (2005) 104408.
[4] H. Nakao et al., J. Phys. Soc. Jpn. 80 (2011) 023711.
[5] S. Asai et al., J. Phys. Soc. Jpn. 80 (2011) 104705.

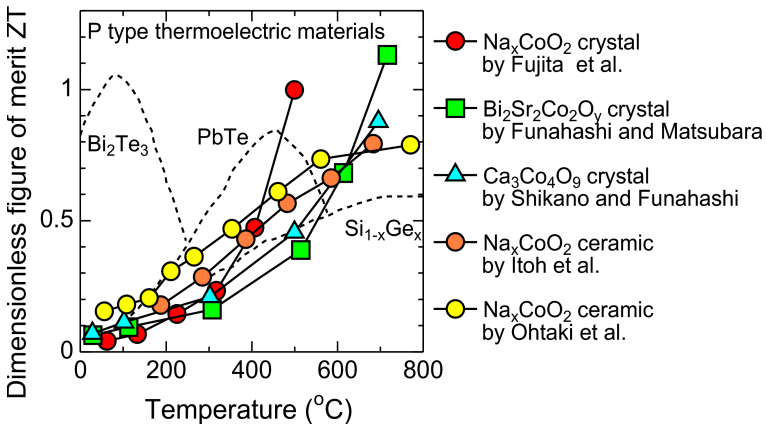

FIG. 1. Dimensionless figure of merit (ZT) for the layered cobalt oxides. The dotted curves represent the ZT values of the p-type conventional thermoelectric materials.

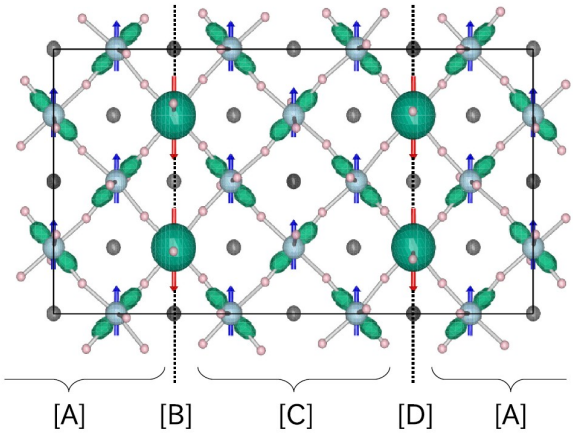

FIG. 2. Spin-state ordering in the A-site ordered perovskite $Sr_3YCo_4O_{10.5}$ [4]. The intermediate spin state ([A] and [C]) and the high spin state ([B] and [D]) are alternately ordered in the CoO_2 plane. Owing to the different spin number, this ordering causes a spontaneous magnetization.