Magnetic and thermoelectric properties of quasi-one-dimensional oxides $A_{n+2}CoB_nO_{3n+3}$ (A=Ca,Sr, B=Co,Rh,Ir; n=1–3)

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(Presented on 7 November 2007; received 10 September 2007; accepted 22 September 2007; published online 16 January 2008)

We studied the magnetic and thermoelectric properties of the homologous series $A_{n+2}CoB_nO_{3n+3}$ (A=Ca,Sr, B=Co,Rh,Ir; n=1–3), which possess one-dimensional chain structures consisting of one CoO_6 trigonal prism and n BO_6 octahedra. Both Ca_3CoRhO_6 and Ca_3CoIrO_6, the n=1 members, exhibited an abrupt drop in the magnetic susceptibility (χ) at around 35 K with decreasing temperature. A broad peak was observed in the χ-T curves at 13 and 5 K, respectively, for the n=2 and 3 samples of the B=Rh series. The change in the magnetic behavior of the B=Rh samples with increasing n is attributable to the increase of interchain distance, while the difference of Ca_3CoRhO_6 and Ca_3CoIrO_6, despite the valence and spin state are the same, may be due to a structural distortion of the latter compound. Thermopower (S) of all three n=1 samples was about 150 μV/K at around 1000 K, and resistivity (ρ) showed semiconductive behavior, with Ca_3CoRhO_6 having the lowest resistivity. As a result, the power factor ($=S^2/\rho$) of Ca_3CoRhO_6 at 1073 K was more than two times larger than that of $Ca_3Co_2O_6$.
 [DOI: 10.1063/1.2828575]

The unit cell of the homologous series $A_{n+2}Co_{n+1}O_{3n+3}$ includes a CoO_3 chain structure, between which the alkaline-earth metal A is located.[1,2] The CoO_3 chain consists of one CoO_6 trigonal prism and n CoO_6 octahedra, which are face sharing and connected one dimensionally. In previous studies, we have investigated systematically the magnetic properties of this one-dimensional (1D) homologous series by varying n from 1 to 5, and have reported the magnetic phase diagram.[3,4] According to those studies, a short-range 1D ferromagnetic (FM) order along the CoO_3 chain appears when the temperature is decreased from room temperature. With further decreasing temperature, a short-range antiferromagnetic (AF) order caused by interchain interaction was found by means of muon spin rotation and relaxation (μ^+SR) measurements. The onset temperature of this short-range AF order decreased systematically with increasing n, most likely because the interchain distance (d_{ic}) increased.[3] We have also studied the thermoelectric properties, and found that the n=2 sample, $Sr_4Co_3O_9$, exhibited the largest power factor.[5] The power factor of this material at 1073 K is 2.3 times larger than that of $Ca_3Co_2O_6$ (n=1), which has been reported to be a promising candidate as a thermoelectric material at high temperature.[6]

Besides changing n, it is also possible to modify $A_{n+2}Co_{n+1}O_{3n+3}$ with an element substitution for Co. In particular, Rh and Ir are known to substitute Co of the CoO_6 octahedron site, and the magnetic properties of the n=1 compounds, Ca_3CoRhO_6 and Ca_3CoIrO_6, have been reported.[7,8] However, little is known about the magnetic properties of the other members of the $A_{n+2}CoB_nO_{3n+3}$ series with B=Rh and Ir. Information about thermoelectric performance of the B=Rh and Ir compounds, including n=1, is also still lacking. Therefore, we studied in this work systematically the magnetic and thermoelectric properties of the $A_{n+2}CoB_nO_{3n+3}$ compounds with n=1–3.

The samples used in this study were prepared by solid state reaction. The starting materials, ACO_3 (A=Ca,Sr), Co_3O_4, Rh, and Ir powders were weighed in a stoichiometric amount, and mixed in a ball mill, High-G BX284EH of Kurimoto, Ltd., with ethanol. The mixtures were then calcined several times at 800–1100 °C for several days in air. The reagents were powdered, then pressed into pellets, and finally sintered at 1200 and 1150 °C in air for 96 h for the B=Rh and Ir compounds, respectively. X-ray diffraction measurements were carried out with a Rigaku diffractometer using Cu $K\alpha$ radiation. Magnetization measurements were performed using a Quantum Design's superconducting quantum iterference device (SQUID) magnetometer. Resistivity was measured with a four-probe method. Thermopower was measured using a homebuilt equipment between 2 and 300 K, and using ZEM2-M10NI of ULVAC between 300 and 1073 K.

The powder x-ray diffraction patterns of Ca_3CoBO_6 confirmed that the samples were single-phase hexagonal structures, with a- and c-axis lengths being in good agreement with the literature data.[7,8] We also succeeded in obtaining

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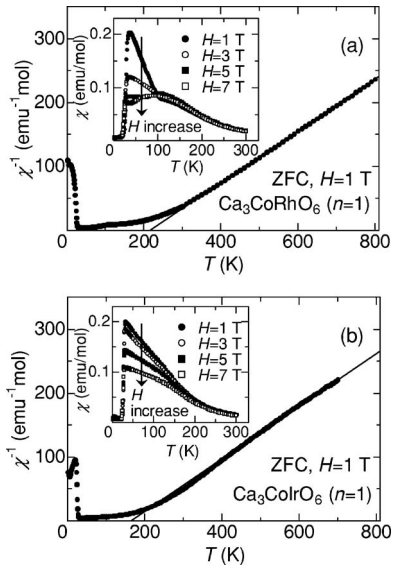

FIG. 1. The temperature dependence of the inverse magnetic susceptibility of (a) Ca_3CoRhO_6 and (b) Ca_3CoIrO_6 measured at $H=1$ T under the ZFC condition. The solid lines are fit to the Curie-Weiss law. The insets show the temperature dependence of magnetic susceptibility measured at various magnetic fields.

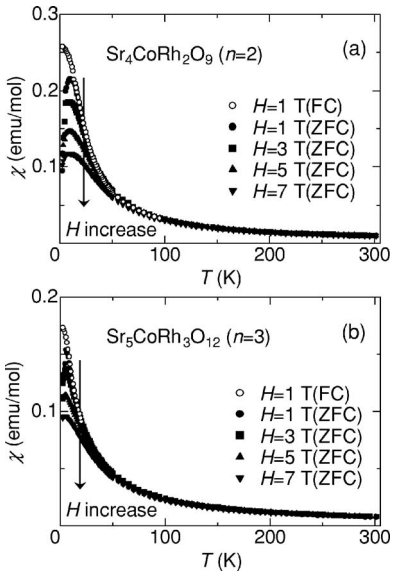

FIG. 2. The temperature dependence of the magnetic susceptibility of (a) $Sr_4CoRh_2O_9$ and (b) $Sr_5CoRh_3O_{12}$ measured at various magnetic fields under the ZFC (closed symbols) and FC (open symbols) conditions.

single-phased samples of $Sr_4CoRh_2O_9$ ($n=2$) and $Sr_5CoRh_3O_{12}$ ($n=3$). The a- and c-axis lengths of the B=Rh samples increased with n. The increase in the a-axis length indicates that d_{ic} increases with n as in the B=Co series, $A_{n+2}Co_{n+1}O_{3n+3}$.[3]

We measured the temperature dependence of the magnetic susceptibility (χ) of $Ca_3Co\mathit{B}O_6$ under the zero-field-cooling (ZFC) condition. The data for temperatures below room temperature have been reported in the literature, and our results are in good agreement with those reports.[7,8] As seen in the inset of Fig. 1(a), a rapid increase of χ was observed below 90 K for Ca_3CoRhO_6 with temperature decreasing. The increase of χ was larger when the applied field was smaller. The transition at 90 K has been argued to correspond to a partially disordered antiferromagnetic (PDA) state.[9] At lower temperatures, an abrupt drop of χ was observed at 35 K, which is considered to be due to spin freezing that induces a frozen PDA state.[9] We also measured the field dependence of magnetization (M-H curve) of the $n=1$ compounds, which were consistent with the published data.[10,11] The magnetization of Ca_3CoRhO_6 at 30, 40, and 50 K showed a plateau, corresponding to 1/3 of the saturation magnetization. The plateau implies the formation of a ferrimagnetic alignment of the FM chains by the applied field. On the other hand, there was a precipitous drop in χ of Ca_3CoIrO_6 at 32 K with temperature decreasing [see the inset of Fig. 1(b)], and χ depended on the magnetic field below about 250 K. However, the increase of χ at low field with decreasing temperature in the temperature range where χ depended on the applied field was not as steep as that of Ca_3CoRhO_6. Furthermore, the M-H curve did not show a plateau at least up to 7 T.

The main panels of Fig. 1 show the temperature dependence of χ^{-1} of (a) Ca_3CoRhO_6 and (b) Ca_3CoIrO_6 measured at $H=1$ T under the ZFC condition. The Curie-Weiss behavior was observed above 350 and 400 K for Ca_3CoRhO_6 and Ca_3CoIrO_6, respectively. The effective magnetic moments were $4.45\mu_B$ and $4.44\mu_B$ for the B=Rh and Ir compounds, respectively, which are close to the theoretical value $4.24\mu_B$ that is calculated by assuming Co of the CoO_6 trigonal prism site to be in a divalent high-spin state, while the B ion of the BO_6 octahedron in a tetravalent low-spin state. These valence states are consistent with the reported x-ray photoemission spectroscopy data.[12] The a-axis length of Ca_3CoIrO_6 was shorter than that of Ca_3CoRhO_6 although Ir has a larger ionic radius than Rh, suggesting that Ca_3CoIrO_6 is structurally distorted to accommodate the large Ir ion. This distortion may be the reason why the magnetic behavior of Ca_3CoIrO_6 is somewhat different from that of Ca_3CoRhO_6 although the valence and spin state are the same.

Figure 2 shows the temperature dependence of χ of (a) $Sr_4CoRh_2O_9$ and (b) $Sr_5CoRh_3O_{12}$ measured at several magnetic fields under the ZFC and field-cooling (FC) conditions. The temperature dependence of χ showed a peak at 13 and 5 K for the $n=2$ and 3 samples, respectively. Because the peak temperature ($=T_p$) of the $n=1$ compound was 35 K, these results show that T_p decreases with increasing n in the $A_{n+2}CoRh_nO_{3n+3}$ series. Furthermore, the M-H curves of $Sr_4CoRh_2O_9$ and $Sr_5CoRh_3O_{12}$ did not show a plateau at least up to 7 T, differently from the $n=1$ sample. We think that the increase in d_{ic} with n is the main reason of the difference in the magnetic behavior with increasing n.

As shown in Fig. 2, χ of the $n=2$ and 3 samples of the B=Rh series depended on the applied field below 70 and 60 K, respectively, and decreased with increasing the field. For the $n=1$ compound, a similar field dependence was observed below 90 K [see the inset of Fig. 1(a)]. In our quite recent μ^+SR study, a sharp decrease in the volume fraction of the paramagnetic phase was observed with temperature decreasing at around 150 K ($n=1$), 80 K ($n=2$), and 60 K ($n=3$).[13] Although the transition temperature deduced from the μ^+SR experiment is somewhat higher than the temperature below which χ displayed a magnetic field dependence,

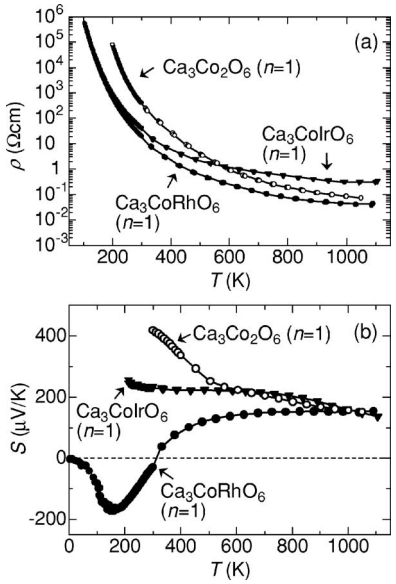

FIG. 3. The temperature dependence of (a) resistivity and (b) thermopower of $Ca_3Co\mathit{B}O_6$. The data of $Ca_3Co_2O_6$ were already reported in Ref. 5.

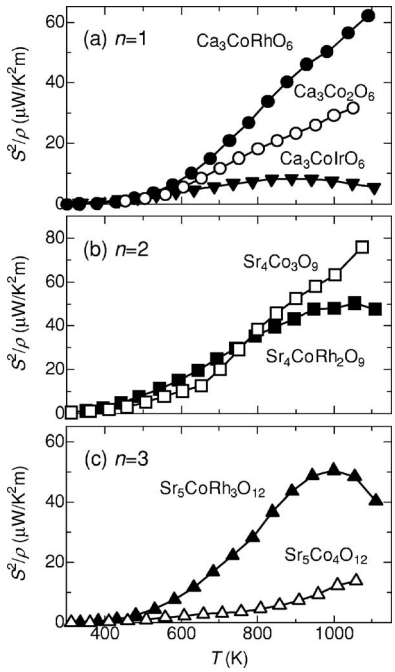

FIG. 4. The temperature dependence of the power factor of $A_{n+2}Co\mathit{B}_nO_{3n+3}$ with (a) n=1, (b) n=2, and (c) n=3, in comparison with our previously reported data of the B=Co compounds (Ref. 5).

they are reasonably close. Therefore, we think that the magnetic field dependence of χ is due to the development of a magnetic order at lower temperatures. Here, it is worth noting that our μ^+SR results seem to be not in support of the PDA state at lower temperatures in Ca_3CoRhO_6.[13] In order to clarify the magnetic state of these compounds, a powder neutron diffraction experiment is in progress.[14]

Figure 3(a) shows the temperature dependence of resistivity of $Ca_3Co\mathit{B}O_6$. All three n=1 samples displayed a semiconductive behavior, and Ca_3CoRhO_6 exhibited the smallest resistivity, 40 mΩ cm at 1073 K. The resistivity of the n=2 and 3 samples of B=Co (Ref. 5) and Rh (not shown) also showed semiconductive behaviors. Figure 3(b) shows the temperature dependence of thermopower of the $Ca_3Co\mathit{B}O_6$ samples. Thermopower at low temperature depended strongly on the B element. The reason of this B dependence is not yet clear but is probably related to the change in the electronic structure.[15] The thermopower at about 1000 K, on the other hand, was almost the same for the three compounds with a value of about 150 μV/K. The thermopower of the n=2 and 3 samples of B=Co (Ref. 5) and Rh (not shown) was in the range of 150–170 μV/K at around 1000 K.

Figure 4 shows the temperature dependence of the power factor of $A_{n+2}Co\mathit{B}_nO_{3n+3}$. The power factors of all samples were small at room temperature, but increased with temperature. Both the resistivity and thermopower tended to decrease with substituting Rh for Co. Because the decrease of resistivity was much larger than thermopower, the power factor of Ca_3CoRhO_6 (n=1) and $Sr_5CoRh_3O_{12}$ (n=3) was larger compared to that of the B=Co samples with the same n. Furthermore, Ca_3CoRhO_6 exhibited the largest power factor among the B=Rh samples studied in this work, although it was slightly smaller than that of $Sr_4Co_3O_9$ (B=Co, n=2). Nevertheless, it was more than two times larger than that of $Ca_3Co_2O_6$ at 1073 K, which was claimed to be a promising candidate as a thermoelectric material at high temperature.[6] Therefore, Ca_3CoRhO_6 can also be considered as a potential candidate as a thermoelectric material at high temperature.

We thank M. Fujiwara of the Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science for helping us in the SQUID measurements with an oven option. T.T. acknowledges gratefully the support of JSPS Research Fellowships for Young Scientists.

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