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LOW TEMPERATURE THERMODYNAMIC PROPERTIES OF $Gd_2SrCo_2O_7$

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Thermodynamic properties of a layered perovskite oxide $Gd_2SrCo_2O_7$ have been studied. Powder X-ray diffraction, electric resistivity, magnetic susceptibility and heat capacity measurements were carried out. The crystal structure was determined as *I*4/*mmm*. The temperature dependence of the magnetic susceptibility was fitted to the Curie-Weiss behavior with antiferromagnetic interaction. Spin state of Co^{3+} ion was derived to be intermediate spin state configuration ($t_{2g}^5 e_g^1$). The spin ordering was observed as a broad anomaly in the heat capacity curve with a peak at 2 K. The measured entropy was 35.47 J $K^{-1}mol^{-1}$, which was 65% of expected value. Thus the spin ordering should not be completed at the lowest temperature 0.2 K covered in the present experiments and/or some short range ordering remains at higher temperatures.

Keywords: *$Gd_2SrCo_2O_7$, $^3He/^4He$ dilution refrigerator, heat capacity, layered perovskite, magnetic ordering*

Introduction

Since the discovery of high-T_c oxide superconductor, much attention has been paid to the intergrowth structures based on layered perovskite. In the case of cobalt mixed oxides, the interesting properties due to spin transitions have been reported in some layered perovskite compounds [1, 2], and recently superconductivity was discovered in lamellar cobalt oxides [3].

In general, the layered perovskite can be represented as Ruddlesden-Popper (RP) series of $\mathbf{A}_{n+1}Co_nO_{3n+1}$ or $\mathbf{A}O\cdot(\mathbf{A}CoO_3)_n$, where n is the number of perovskite blocks composed by two-dimensional layers of CoO_6 corner-sharing octahedra separated by rocksalt **A**O layers [4, 5], and **A** is rare earth element. A number of studies have been made on the crystal structure, magnetic and transport properties for the compounds of n=1 (that is K_2NiF_4-type structure) and of n=∞ (that is perovskite ABO_3-type structure) [1–3, 6–13]. On the other hand, only a limited number of studies have been reported on the compounds of n=2 and n=3 [14, 15]. The high temperature transport and magnetic properties have been studied of $Gd_2SrCo_2O_7$ by Siwen and Yufang [15]. However, no detailed study has been reported for the properties of low temperature region.

In the present study, we synthesized $Gd_2SrCo_2O_7$ and determined the atomic coordinates using the results of synchrotron radiation powder X-ray diffraction. The spin state of Co^{3+} ion was investigated from magnetic susceptibility measurement. The heat capacity was measured and the magnetic contribution due to the spin ordering process was discussed.

Experimental

The samples of $Gd_{2-x}Sr_{1+x}Co_2O_7$ (x=0.0, 0.1 and –0.1) were synthesized by the following procedure. The powders of Gd_2O_3 (Rare Metallic Co., Ltd., nominal purity of 99.99%), Co_2O_3 (Rare Metallic Co., Ltd., nominal purity of 99.9%) and $SrCO_3$ (Wako Pure Chemical Industry, Ltd., nominal purity of 99.99%) were mixed in the ratio of the chemical formula with an alumina mortar and a pestle. The mixture was pressed into a disk under 25 MPa, and then it was calcinated at 1173 K for 18 h in oxygen gas flow of atmospheric pressure. The calcined disk was ground, and pressed into a disk again under 25 MPa, and then it was heated at 1250 K for 18 h in the oxygen gas flow. Finally, the disk was heated at 1380 K for 24 h in the oxygen gas flow, and then it was cooled down slowly to room temperature in the electric furnace.

The high energy X-ray powder diffraction experiment was carried out using BL02B2 beam line at SPring-8 of the Japan Synchrotron Radiation Research Institute. The powdered sample was sealed into a Pyrex glass tube of 0.3 mm inside diameter. High energy X-ray with wavelength λ=0.065321 nm was used. The diffraction patterns were obtained for the samples of x=0.0, 0.1 and –0.1 from 10 to 70° in 2θ range. The results obtained at room temperature are shown in Fig. 1, where impurity phases of $GdSrCoO_4$ and Gd_2O_3 are observed in the samples of $Gd_{1.9}Sr_{1.1}Co_2O_7$ and $Gd_{2.1}Sr_{0.9}Co_2O_7$. In the case of $Gd_2SrCo_2O_7$, no impurity is detected, and further measurements were made only for this sample. The precise chemical composition was determined to be

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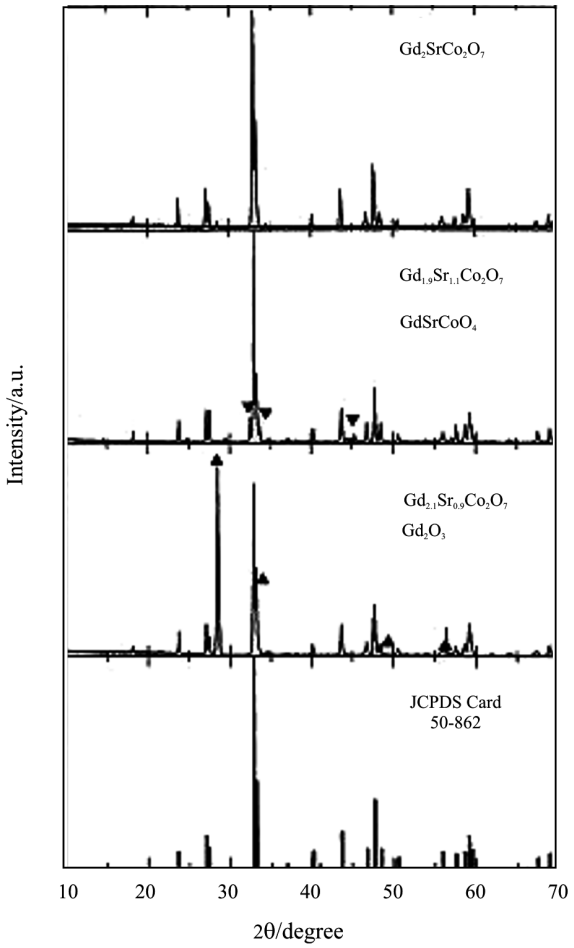

Fig. 1 Powder X-ray diffraction patterns of $Gd_{2-x}Sr_{1+x}Co_2O_7$ (x=0.0, 0.1 and –0.1) at room temperature. The single phase is obtained only for $Gd_2SrCo_2O_7$

$Gd_{1.99}Sr_{0.99}Co_2O_{7-\delta}$ by ICP (Inductively Coupled Plasma) analysis. The structural analysis was made by Rietveld method using RIETAN-2000 program [16].

Electric resistivity measurements were carried out with 4-probes dc method in the temperature range between 170 and 300 K. The gold wires of 0.05 mm in diameter were connected to the sintered sample (the size was 1.0×2.5×9.0 mm) with silver paste.

The magnetic susceptibility measurements were made for the powdered sample of 100 mg using a SQUID magnetometer (MPMS, Quantum Design Co., Ltd.) in the temperature range between 5 and 300 K under the magnetic field of 0.01 T.

The heat capacity measurements were made for a sintered sample of 0.94 mg using a home-made relaxation-type calorimeter mounted with RuO_2 thermometer in a $^3He/^4He$ dilution refrigerator for the temperature range between 0.2 and 4 K [17]. At higher temperatures from 2 to 300 K, the heat capacity was measured using a commercial apparatus (PPMS, Quantum Design Co., Ltd.) with relaxation method. The amount of the sintered sample used for the heat capacity measurements was 2.0 mg.

Results and discussion

The X-ray diffraction pattern obtained for the single phase sample of $Gd_{1.99}Sr_{0.99}Co_2O_{7-\delta}$ was analyzed, and all the peaks were successfully indexed on the tetragonal $Sr_3Ti_2O_7$-type structure of $I4/mmm$. The structure parameters have been determined by Rietveld method at room temperature. Atomic parameters and some resultant parameters of the analysis are given in Table 1. The present lattice constants agree with the literature values by Siwen and Yufang [15].

The results of electric resistivity measurements show that the temperature dependence is of a semiconductor type in the whole temperature region covered by the present experiments. From the plots of logarithm of resistivity *vs.* T^{-1}, the activation energy is estimated as 9.5 kJ mol^{-1}.

The temperature dependence of the magnetic susceptibility can be fitted to the Curie-Weiss law with Weiss temperature of θ=–9.81 K in the whole temperature range between 5 and 300 K, which is shown in Fig. 2. The results indicate that the magnetic states of Gd^{3+} and Co^{3+} ions were unchanged in this temperature region and the dominant magnetic exchange interaction should be antiferromagnetic. As-

Table 1 Atomic parameters and some resultant parameters of $Gd_2SrCo_2O_7$ (a=0.3804 nm, c=1.9388 nm, R_{wp}=7.29%, R_I=4.19%, R_F=2.41%)

Atom	site	g	x	y	z	B/nm^2
Gd(1)	2*b*	0.67	0	0	0.5	0.0086
Sr(1)	2*b*	0.33	0	0	0.5	0.0086
Gd(2)	4e	0.67	0	0	0.3191	0.0082
Sr(2)	4e	0.33	0	0	0.3191	0.0082
Co	4e	1.0	0	0	0.0976	0.0026
O(1)	2*a*	1.0	0	0	0	0.0218
O(2)	4e	1.0	0	0	0.1911	0.0218
O(3)	8*g*	1.0	0	0.5	0.1012	0.0218

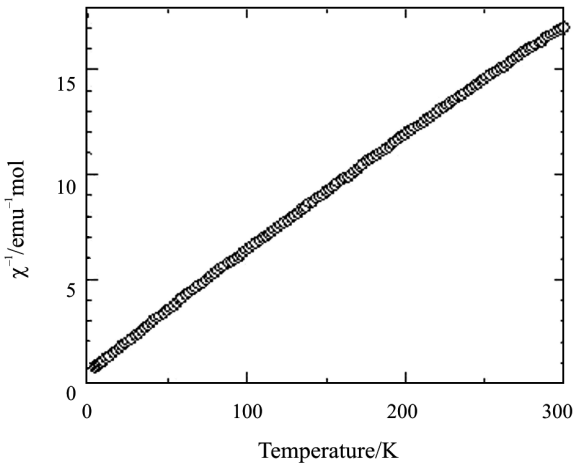

Fig. 2 Temperature dependence of inverse magnetic susceptibility $1/\chi$ of $Gd_2SrCo_2O_7$. The data can be fitted to the Curie–Weiss equation in the whole temperature range between 5 and 300 K

suming the effective magnetic moment of free Gd^{3+} ion, the effective magnetic moment for Co^{3+} ion is calculated to be 3.05 μ_B. This effective magnetic moment agrees with the value estimated by assuming S=1 spin state of Co^{3+} ion (2.83 μ_B). Thus, the spin state in the present compound is considered to be of an intermediate spin state of configuration formed with Co^{3+} ions ($t_{2g}^5 e_g^1$). It has been reported that the tetragonally distorted octahedral site is stabilized in such a configuration [18, 19].

The heat capacity measured with PPMS in the temperature range between 2 and 300 K is shown in Fig. 3. A heat capacity anomaly is observed below about 20 K. To measure the heat capacity at lower temperatures, the home-made relaxation type calorimeter set in a $^3He/^4He$ dilution refrigerator was used down to 0.2 K. The results of the low temperature region are shown in Fig. 4. The solid line is the lattice contribution, which is the heat capacity extrapolated from higher temperatures above 22 K, where no phase transition exists. The lattice contribution is calculated by fitting the heat capacity above 22 K to the combinations of Debye and Einstein functions. The excess heat capacity due to the magnetic contribution was obtained by subtracting the lattice heat capacity from the measured heat capacity. The magnetic entropy was calculated to be 34.58 J K^{-1} mol^{-1} from the excess heat capacity. In general, compounds containing Gd^{3+} or Co^{3+} ion should exhibit heat capacity anomaly due to the spin ordering in the low temperature region. The magnetic entropy of spin ordering for Gd^{3+} ion per mole is expected to be Rln8. The results of the

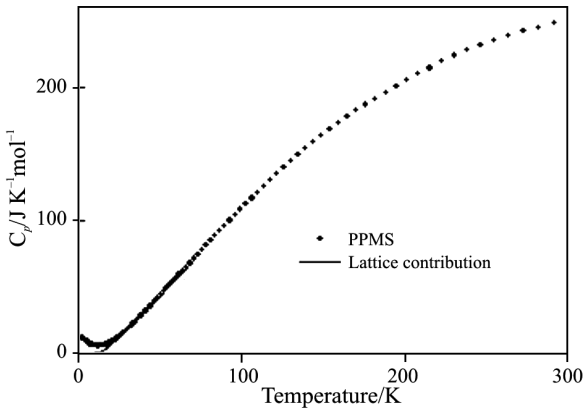

Fig. 3 Molar heat capacity of $Gd_2SrCo_2O_7$ measured with PPMS in the temperature range between 2 and 300 K. Solid line shows the lattice contribution

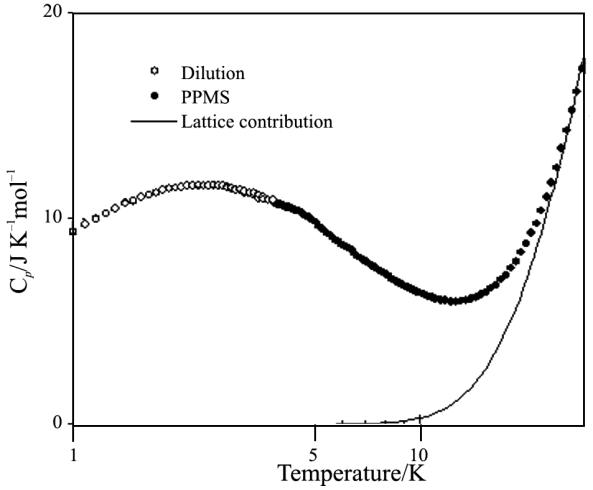

Fig. 4 Molar heat capacity of $Gd_2SrCo_2O_7$ in the low temperature range. The data down to 0.2 K were obtained by a home-made calorimeter set in a $^3He/^4He$ dilution refrigerator (denoted by open circles). The closed circles are those obtained by PPMS. Solid line shows the lattice contribution

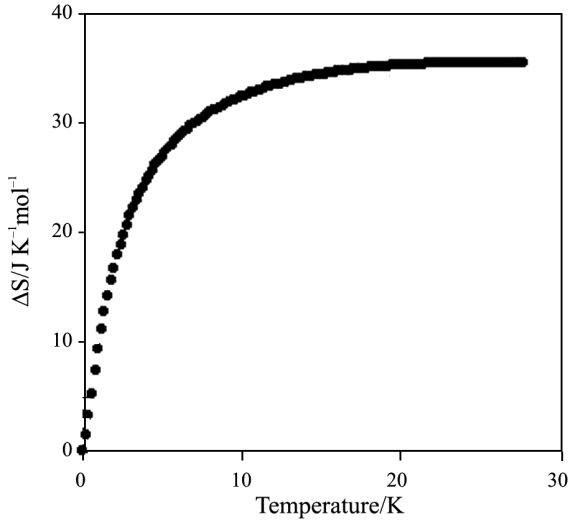

Fig. 5 Temperature dependence of magnetic entropy ΔS of $Gd_2SrCo_2O_7$

magnetic susceptibility measurement indicate that the Co^{3+} ion is in the intermediate state of S=1. Consequently, the magnetic entropy of spin ordering for Co^{3+} ion per mole is expected to be Rln3. Therefore, the total magnetic entropy of $Gd_2SrCo_2O_7$ is expected to be $2R$ln8+$2R$ln3=52.85 J K^{-1} mol^{-1}. However, the experimental value of magnetic entropy 35.48 J K^{-1} mol^{-1} is only about 65% of the theoretical value. These results indicate that the magnetic spins are still not completely ordered at 0.2 K, and/or some short range ordering remains at higher temperatures.

Conclusions

The samples of $Gd_{2-x}Sr_{1+x}Co_2O_7$ (x=0.0, 0.1 and –0.1) were synthesized, and only $Gd_2SrCo_2O_7$ (precisely determined as $Gd_{1.99}Sr_{0.99}Co_2O_{7-\delta}$) was successfully prepared in single phase. No solid solution range was observed in $Gd_{2-x}Sr_{1+x}Co_2O_7$, as the samples of x=0.1 and –0.1 were not prepared as a single phase. The crystal structure, electric, magnetic, and thermodynamic properties were investigated for the sample of $Gd_{1.99}Sr_{0.99}Co_2O_{7-\delta}$. The synchrotron radiation powder X-ray diffraction showed that the compound had n=2 RP layered perovskite structure. The results of magnetic measurements indicate an intermediate spin state configuration of Co^{3+} ions ($t_{2g}^5e_g^1$), assuming S=1 spin state of Co^{3+} ion. A broad heat capacity anomaly was observed at 2 K, which should be associated with the magnetic ordering. The magnetic entropy calculated from the heat capacity anomaly is only about 65% of the theoretical value.

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