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Magnetic and neutron diffraction study on iridium(IV) perovskites Sr_2LnIrO_6 (Ln = Ce, Tb)

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Abstract. Powder neutron diffraction measurements have been performed for two tetravalent iridium perovskites, Sr_2CeIrO_6 ($T_N = 21$ K) and Sr_2TbIrO_6 ($T_N = 51$ K). It is found that moments of Tb^{4+} in these ordered perovskites are stacked antiferromagnetically along the *c*-axis, and the magnetic structure is of type I. The ordered magnetic moment of Tb^{4+} is 4.96 μ_B at 28 K and 6.60 μ_B at 2 K. From magnetic susceptibility measurements on $Sr_2Ce_xTb_{1-x}IrO_6$, the antiferromagnetic transition temperatures decrease greatly with decreasing Tb^{4+} ion, which indicates that the pathway of such interactions must involve the Tb^{4+} ions.

1. Introduction

The perovskite-type oxides have the general formula ABO_3, in which A represents a large electropositive cation and B represents a small transition metal ion. The perovskite structure can be described as a framework of corner-shared BO_6 octahedra which contains A cations at 12-coordinate sites. Double perovskite-type oxides have the formula $A_2B'B''O_6$, in which the primes indicate the different ions in different oxidation states, and in some cases, the cations at the B sites, B′ and B″, regularly order, i.e., 1:1 arrangements of B′ and B″ ions have been observed over the six-coordinate B sites. Figure 1 illustrates the typical crystal structure of double perovskite, Sr_2LnIrO_6. Since the B cations generally determine the physical properties of perovskites, different kinds of B′ and B″ ion should show a variety of the physical properties of double perovskites.

Previously, we reported crystal structures and magnetic properties of iridium perovskites Sr_2LnIrO_6 (Ln = Ce, Sm–Lu) [1]. Through their x-ray diffraction measurements, we have found that although the lattice parameters for Sr_2LnIrO_6 increase smoothly with the ionic radius of Ln^{3+} ion, those for Sr_2CeIrO_6 and Sr_2TbIrO_6 deviated greatly from this trend. For these experimental results, we have discussed that the Ce and Tb ions are not in the trivalent state, but in the tetravalent state. This consideration has been also supported by the fact that the effective magnetic moment of the terbium ion (7.97 μ_B) obtained from the susceptibility measurements for Sr_2TbIrO_6 accords with the theoretical moment for the Tb^{4+} ion (7.94 μ_B) (for the Tb^{3+} ion, the moment is calculated to be 9.72 μ_B). The results of the magnetic susceptibility measurements are that these Sr_2LnIrO_6 compounds are paramagnetic and that among them, Sr_2CeIrO_6 and Sr_2TbIrO_6 show the antiferromagntic transition at 21 and 51 K,

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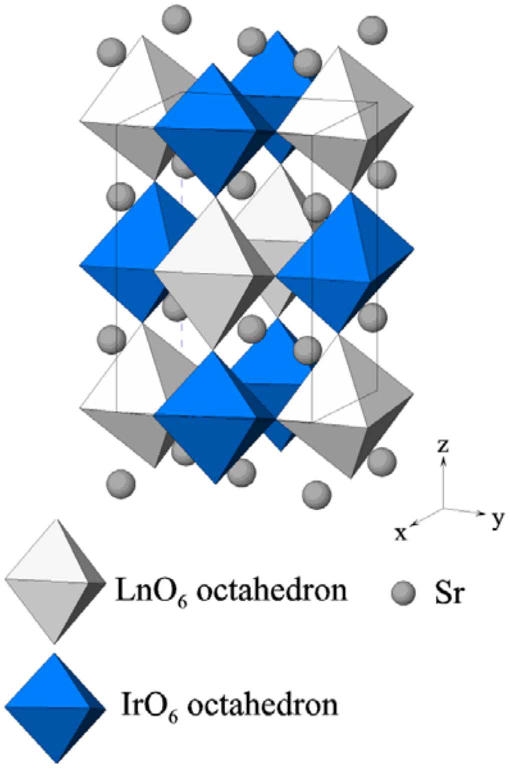

Figure 1. The crystal structure of Sr_2LnIrO_6.

respectively. Figures 2 and 3 show the temperature dependence of magnetic susceptibilities for these compounds. In addition to the magnetic transition at 51 K, Sr_2TbIrO_6 shows another anomaly at 27 K in its magnetic susceptibility–temperature curve (see figure 3). As far as we know, there was no report on the magnetic properties of compounds in which iridium and lanthanide elements are contained. Very recently, we have published magnetic properties of A_2RIrO_6 (A = Sr, Ba; R = Sc, Y, La, Lu) [2] in which only Ir^{5+} are magnetic ions. They are all paramagnetic down to 2 K, i.e. no magnetic cooperative phenomena have been found in these compounds.

In this paper, we focus our attention on the magnetic properties of Sr_2CeIrO_6 and Sr_2TbIrO_6. In the Sr_2TbIrO_6, there are two kinds of magnetic ion, i.e. Tb^{4+} and Ir^{4+} ions. The electronic structures of these ions are $[Xe]4f^7$ and $[Xe]4f^{14}5d^5$, respectively, where [Xe] is the xenon core. Therefore, we can expect to observe magnetic cooperative phenomena caused by these 4f and 5d electrons. Battle *et al* reported magnetic properties of double-perovskite-type oxides such as Ca_2LaRuO_6, Sr_2YRuO_6, Ca_2HoRuO_6, Ca_2YRuO_6 [3–6], and determined their magnetic structures to be type I antiferromagnetic.

We have performed powder neutron diffraction measurements for both the compounds to elucidate their magnetic structures in the antiferromagentic state. In addition, magnetic susceptibilities of solid solutions $Sr_2Ce_xTb_{1-x}IrO_6$ have been measured to clarify the anomaly found in the susceptibility of Sr_2TbIrO_6 and to obtain information on the magnetic interaction between 5d and 4f electrons.

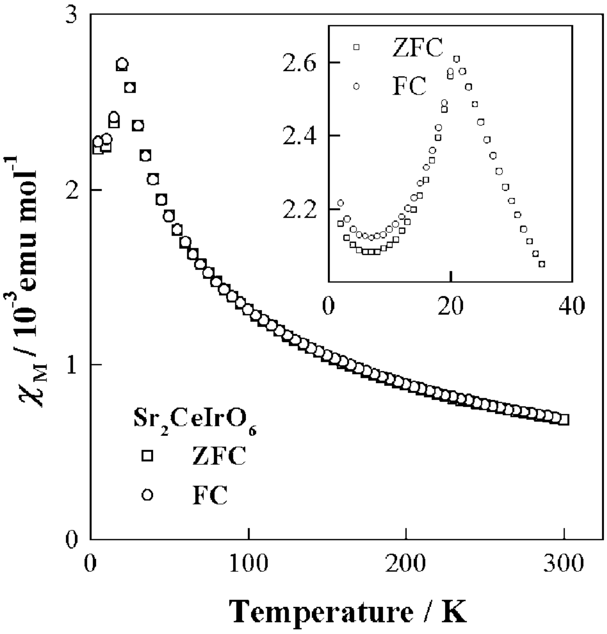

Figure 2. Temperature dependence of the magnetic susceptibilities of Sr_2CeIrO_6.

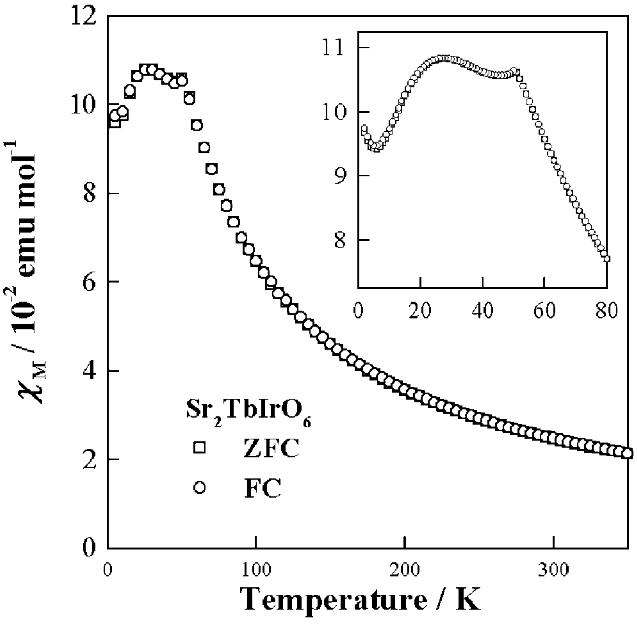

Figure 3. Temperature dependence of the magnetic susceptibilities of Sr_2TbIrO_6.

2. Experiment

Sintered materials of $Sr_2Ce_xTb_{1-x}IrO_6$ ($x = 0, 0.1, 0.2, \ldots, 1.0$) were prepared. Powders of $SrCO_3$, CeO_2, Tb_4O_7 and Ir were weighed in the appropriate metal ratios, and were ground intimately in an agate mortar. The mixtures were pressed into pellets and then calcined in air at 900 °C for 12 h. The samples were heated again in air at 1200 °C for 72–96 h with several interval grindings.

Powder x-ray diffraction profiles for these solid solutions were recorded, with Cu Kα radiation on a Rigaku RINT 2000 diffractometer equipped with a curved graphite monochromator in the range $10^\circ \leqslant \theta \leqslant 120^\circ$ at intervals of 0.02°. The structures were refined with the Rietveld analysis method, using the Rietan program [8].

Powder neutron diffraction profiles for Sr_2CeIrO_6 and Sr_2TbIrO_6 were measured in the range $3^\circ \leqslant \theta \leqslant 153^\circ$ at intervals of 0.1° at wavelength of 1.819 Å. Measurements were performed by the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, of the institute for Materials Research, Tohoku University [9], installed at the JRR-3M reactor in Japan Atomic Energy Research Institute Tokai, Japan. Since Sr_2CeIrO_6 shows an antiferromagnetic transition temperature at $T_N = 21$ K, measurements were made both at 2 K ($T < T_N$) and at 30 K ($T > T_N$). For Sr_2TbIrO_6 showing both the antiferromagnetic transition at $T_N = 51$ K and a certain anomaly at about $T_A = 27$ K, measurements were made at 2 K ($T < T_A < T_N$), 28 K ($T_A < T < T_N$) and 60 K ($T_A < T_N < T$).

The temperature dependence of magnetic susceptibilities for $Sr_2Ce_xTb_{1-x}IrO_6$ ($x = 0, 0.1, 0.2, \ldots, 1.0$) was measured with a SQUID (Quantum Design, MPMS model) under the zero-field-cooled condition (ZFC). It was measured on heating the samples to 80 K after zero-field cooling to 2 K. The applied magnetic field was 0.1 T. Magnetic susceptibility for these compounds does not depend on the applied magnetic field up to 5.0 T. The temperature dependence of the susceptibility under the field-cooled condition (FC) was not measured, because we have previously found that there was no divergence between the ZFC and the FC magnetic susceptibilities for these compounds [1].

3. Results and discussion

3.1. Neutron diffraction measurements

3.1.1. Sr_2CeIrO_6. Our previous x-ray diffraction measurements on Sr_2CeIrO_6 and Sr_2TbIrO_6 show that these two compounds both have the monoclinic perovskite structure with the space group $P2_1/n$. Figure 4 shows the neutron diffraction profiles for Sr_2CeIrO_6 measured at 2 and 30 K. The results of the crystal structure determination on Sr_2CeIrO_6 by the present neutron diffraction measurements are given in table 1 together with those by the x-ray diffraction measurements. The results of neutron diffraction measurements performed at 2 and 30 K agree well with the x-ray diffraction results, which means that the crystal phase transition does not occur at low temperatures. Atomic positions of strontium occupying the A site of the perovskite structure are well in accordance between x-ray diffraction measurement and neutron diffraction measurement. But the atomic positions of oxygen are a little in disagreement between these measurements. We consider that the results by neutron diffraction measurements are more reliable, because x-ray diffraction measurements have a disadvantage for determining the positions of light atoms. With decreasing temperature (from room temperature to 30 K), lattice parameters of Sr_2CeIrO_6 decrease.

Since Sr_2CeIrO_6 shows the antiferromagnetic transition at 21 K, magnetic Bragg peaks should appear in the neutron diffraction profile measured at 2 K. However, no difference in the neutron diffraction profiles measured at 2 K and at 30 K was observed (figure 4). Currie *et al* [7] reported that magnetic Bragg peaks were not observed in the neutron diffraction measurements of a double perovskite La_2CoIrO_6 which is isostructural with our samples

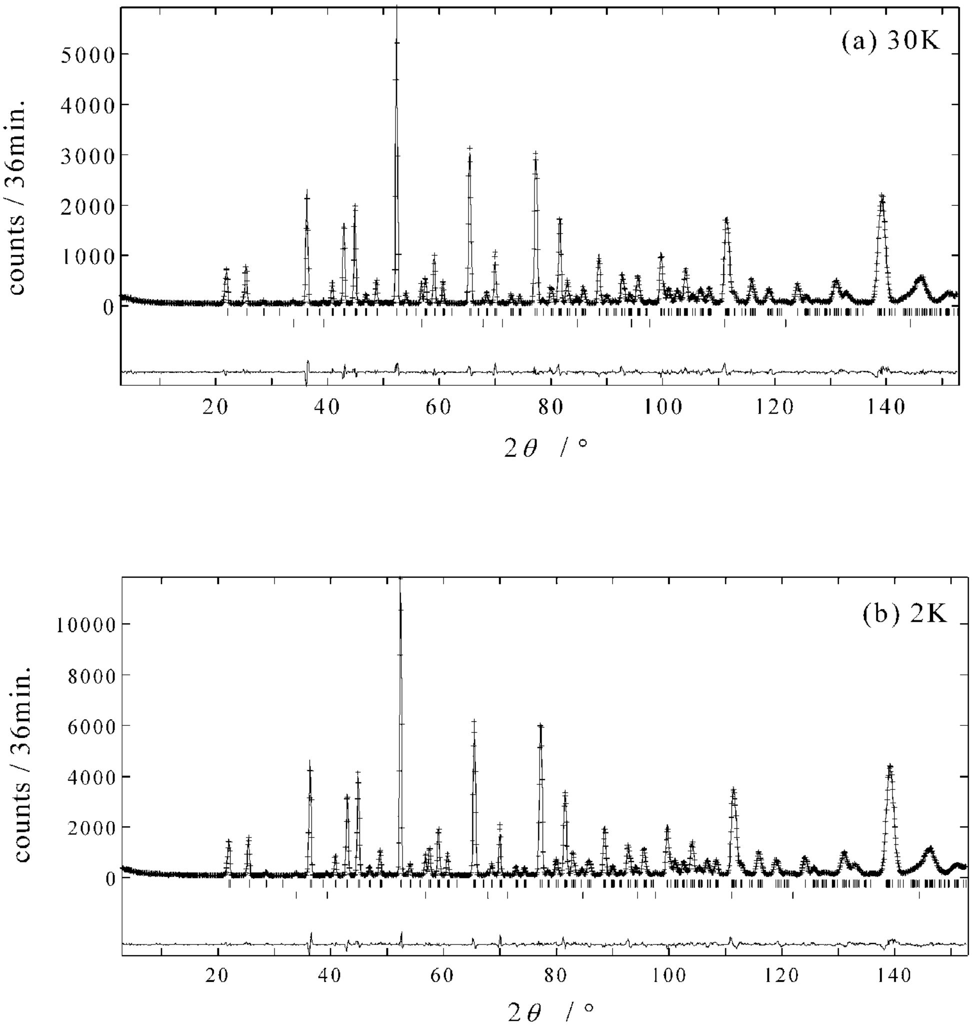

Figure 4. Neutron diffraction profiles for Sr_2CeIrO_6 at (a) 30 K and (b) 2 K.

Sr_2LnIrO_6 (Ln = Ce, Tb). We consider that since the magnetic moment of the Ir^{4+} ion which is the only magnetic ion in Sr_2CeIrO_6 is very small, magnetic diffraction peaks are not detected.

3.1.2. Sr_2TbIrO_6. The magnetic susceptibility measurement on Sr_2TbIrO_6 shows the antiferromagnetic transition at 51 K (T_N) and another anomaly at about 27 K (T_A). Therefore, we performed our neutron diffraction measurements at three temperatures, 60 K ($T_N < T$), 28 K ($T_A < T < T_N$) and 2 K ($T < T_A$). Figure 5 shows the observed and calculated neutron diffraction profiles. The atomic parameters for Sr_2TbIrO_6 after the refinement of the neutron diffraction profiles are given in table 2 together with those by the x-ray diffraction measurements. All the diffraction peaks measured at 60 K can be indexed in a monoclinic unit cell with space group $P2_1/n$. In the profiles measured at 28 and at 2 K, magnetic Bragg reflections in addition to the nuclear Bragg reflections appear. These magnetic Bragg peaks are due to the alignment of the Tb^{4+} moment. Magnetic Bragg reflections due to the alignment of

Table 1. Crystal and magnetic structure data for Sr_2CeIrO_6.

Atoms	Position	x	y	z
X-ray diffraction at RT				
$a = 5.8341(3)$ Å $b = 5.8436(3)$ Å $c = 8.2559(6)$ Å $\beta = 90.195(4)^\circ$ $V = 281.46(3)$ Å^3				
$R_{wp} = 12.09\%$ $R_I = 2.48\%$ $R_F = 2.35\%$				
Sr	4e	0.497(2)	0.530(1)	0.255(2)
Ce	2d	0.5	0.0	0.0
Ir	2c	0.5	0.0	0.5
O1	4e	0.26(1)	0.29(1)	0.04(1)
O2	4e	0.19(1)	0.77(1)	0.02(1)
O3	4e	0.59(1)	−0.01(1)	0.26(1)
Neutron diffraction at 30 K				
$a = 5.8165(3)$ Å $b = 5.8389(3)$ Å $c = 8.2337(5)$ Å $\beta = 90.227(4)^\circ$ $V = 279.64(3)$ Å^3				
$Q = 1.71(5)$ $R_{wp} = 9.07\%$ $R_I = 1.50\%$ $R_F = 0.75\%$				
Sr	4e	0.492(1)	0.532(1)	0.252(2)
Ce	2d	0.5	0.0	0.0
Ir	2c	0.5	0.0	0.5
O1	4e	0.273(1)	0.296(2)	0.038(1)
O2	4e	0.198(2)	0.774(2)	0.040(1)
O3	4e	0.573(2)	−0.016(1)	0.263(1)
Neutron diffraction at 2 K				
$a = 5.8180(3)$ Å $b = 5.8402(2)$ Å $c = 8.2355(4)$ Å $\beta = 90.225(3)^\circ$ $V = 279.82(2)$ Å^3				
$Q = 1.83(5)$ $R_{wp} = 9.25\%$ $R_I = 1.41\%$ $R_F = 0.71\%$				
Sr	4e	0.492(1)	0.532(1)	0.252(1)
Ce	2d	0.5	0.0	0.0
Ir	2c	0.5	0.0	0.5
O1	4e	0.273(1)	0.296(2)	0.038(1)
O2	4e	0.197(1)	0.775(2)	0.041(1)
O3	4e	0.572(2)	−0.016(1)	0.263(1)

Definitions of reliability factors R_{WP}, R_I and R_F are given as follows, $R_{WP} = [\sum w(|F(o)| - |F(c)|)^2 / \sum w|F(o)|^2]^{1/2}$, $R_I = \sum |I_k(o) - I_k(c)| / \sum I_k(o)$ and $R_F = \sum |[I_k(o)]^{1/2} - [I_k(c)]^{1/2}| / \sum [I_k(o)]^{1/2}$.

the magnetic moments of Ir^{4+} ions do not appear experimentally, which is in accordance with the result for Sr_2CeIrO_6. The large (100) and (010) peaks ($2\theta \cong 18.2^\circ$) are observed in the profiles measured at 28 and at 2 K, but the intensity of the (001) diffraction ($2\theta \cong 12.8^\circ$) is very weak. This fact indicates that the magnetic moments of Sr_2TbIrO_6 are aligned almost along the *c*-axis. We expect that the magnetic structure is of the antiferromagnetic type I (figure 6) from the magnetic Bragg peaks. The Rietveld analysis assuming the type I magnetic structure gives the most reliable results.

A Tb^{4+} ion has 12 nearest neighbour Tb^{4+} ions (NN) and six next-nearest neighbours (NNN). The type I magnetic structure consists of eight nearest neighbours antiferromagnetically coupled to the central ion, four nearest neighbours in the *c* planar ferromagnetically coupled and all six next-nearest neighbours ferromagnetically coupled. Battle *et al* [3–6] discussed the dominant magnetic interactions in such a structure, which was either those between NN or those between NNN for Ca_2LaRuO_6, Ba_2LaRuO_6, Ca_2LaRuO_6, Sr_2YRuO_6. Since two kinds of magnetic ion, Ir and Tb, are involved in the case of Sr_2TbIrO_6, the interaction between Ir and Tb should be considered, which means that the dominant pathway of magnetic interactions is very complicated.

The ordered magnetic moments at 28 and at 2 K are calculated to be 4.94 and 6.60 μ_B, respectively. The saturated magnetic moment for the Tb^{4+} ion ($4f^7$) is 7.0 μ_B. Although the

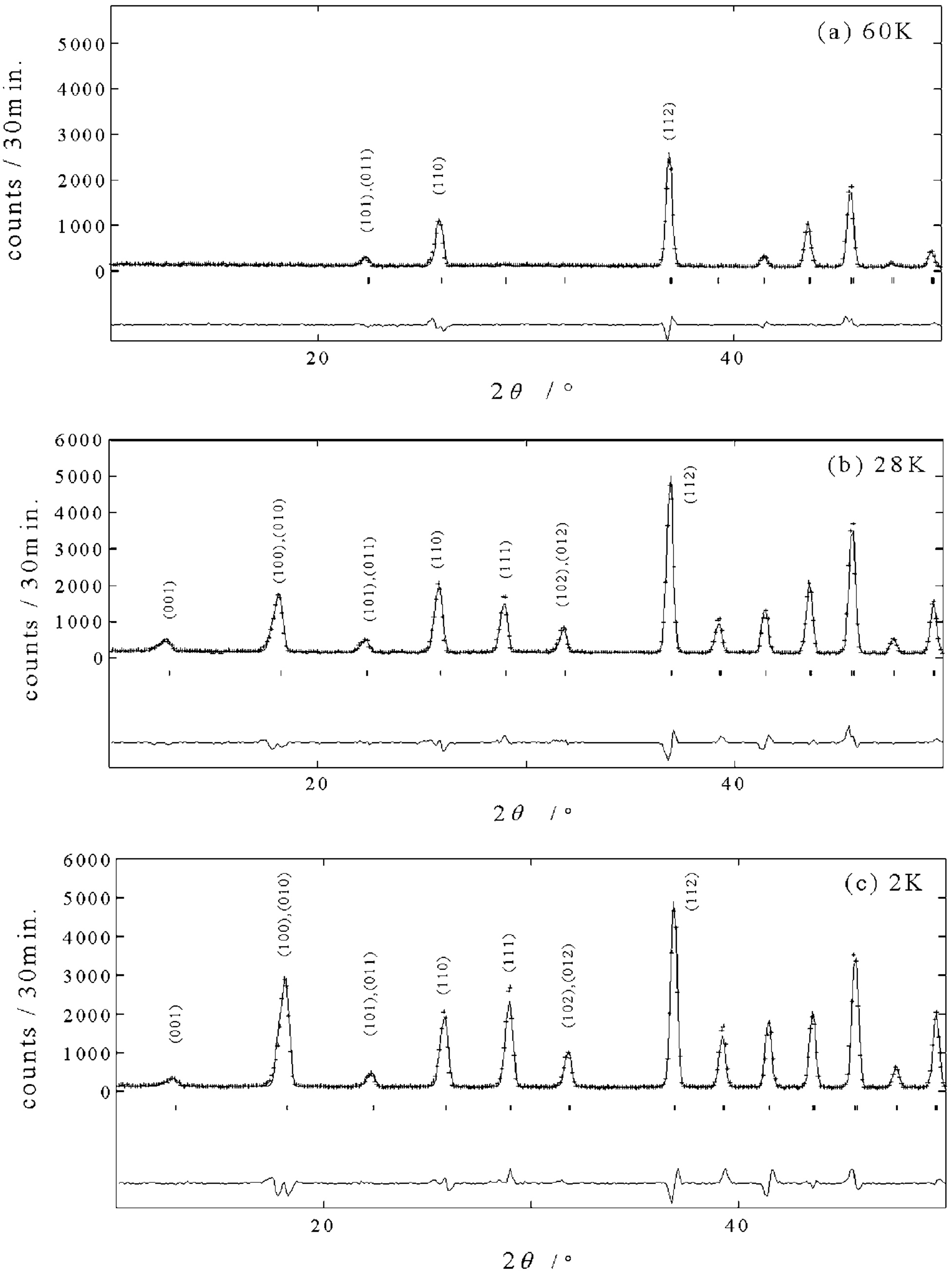

Figure 5. Neutron diffraction profiles for Sr_2TbIrO_6 at (a) 60 K, (b) 28 K and (c) 2 K.

moment at 2 K is larger than that at 28 K, the intensity of the (001) reflection at 2 K is weaker than that at 28 K (see figure 7). This result indicates that the angle between the direction of the moment and the c-axis at 2 K is smaller than that at 28 K, and that the magnetic moment of the Tb^{4+} ion orders remarkably with decreasing temperature. Although the anomaly has been found at 27 K in the susceptibility–temperature curve, there is no difference in the diffraction

Table 2. Crystal and magnetic structure data for Sr_2TbIrO_6.

Atoms	Position	x	y	z
X-ray diffraction at RT				
$a = 5.7604(2)$ Å $b = 5.7506(2)$ Å $c = 8.1371(3)$ Å $\beta = 90.089(2)^\circ$ $V = 269.55(1)$ Å^3				
$R_{wp} = 9.72\%$ $R_I = 1.75\%$ $R_F = 2.10\%$				
Sr	4e	0.492(1)	0.521(1)	0.247(1)
Tb	2d	0.5	0.0	0.0
Ir	2c	0.5	0.0	0.5
O1	4e	0.28(1)	0.29(1)	0.04(1)
O2	4e	0.22(1)	0.76(1)	0.02(1)
O3	4e	0.56(1)	−0.01(1)	0.26(1)
Neutron diffraction at 60 K				
$a = 5.7431(4)$ Å $b = 5.7440(4)$ Å $c = 8.1147(5)$ Å $\beta = 90.148(5)^\circ$ $V = 267.69(3)$ Å^3				
$Q = 0.61(6)$ $R_{wp} = 10.30\%$ $R_I = 2.66\%$ $R_F = 1.39\%$				
Sr	4e	0.495(2)	0.525(1)	0.250(2)
Tb	2d	0.5	0.0	0.0
Ir	2c	0.5	0.0	0.5
O1	4e	0.272(2)	0.284(3)	0.036(2)
O2	4e	0.209(2)	0.780(3)	0.032(2)
O3	4e	0.560(2)	−0.012(2)	0.259(2)
Neutron diffraction at 28 K				
$a = 5.7464(4)$ Å $b = 5.7463(3)$ Å $c = 8.1234(5)$ Å $\beta = 90.134(5)^\circ$ $V = 267.79(3)$ Å^3				
$Q = 0.79(4)$ $R_{wp} = 8.98\%$ $R_I = 3.22\%$ $R_F = 1.96\%$				
Sr	4e	0.494(2)	0.529(1)	0.246(1)
Tb	2d	0.5	0.0	0.0
Ir	2c	0.5	0.0	0.5
O1	4e	0.273(2)	0.288(2)	0.032(1)
O2	4e	0.212(2)	0.780(2)	0.029(1)
O3	4e	0.566(2)	−0.013(2)	0.259(1)
Magnetic moment: 4.96 μ_B				
Angle between the moment and the c-axis: 28.67°				
Neutron diffraction at 2 K				
$a = 5.7464(4)$ Å $b = 5.7461(3)$ Å $c = 8.1243(4)$ Å $\beta = 90.143(5)^\circ$ $V = 267.95(3)$ Å^3				
$Q = 1.03(5)$ $R_{wp} = 9.92\%$ $R_I = 3.21\%$ $R_F = 1.66\%$				
Sr	4e	0.494(2)	0.530(1)	0.247(2)
Tb	2d	0.5	0.0	0.0
Ir	2c	0.5	0.0	0.5
O1	4e	0.273(2)	0.289(2)	0.031(1)
O2	4e	0.213(2)	0.779(2)	0.029(1)
O3	4e	0.566(2)	−0.015(1)	0.259(1)
Magnetic moment: 6.60 μ_B				
Angle between the moment and the c-axis: 16.96°				

profiles between that at 2 K and at 28 K, i.e. no new magnetic Bragg peaks appear between them.

To obtain information on the anomaly in the magnetic susceptibility, we have measured the temperature dependence of the diffraction peaks for Sr_2TbIrO_6 in the temperature range of 2 K to 60 K at intervals of 2–3 K. Unfortunately, no remarkable change was found in the neutron diffraction profiles. We believe that since the anomaly is found as a broad maximum in the susceptibility–temperature curve, the corresponding magnetic Bragg peaks are very weak and therefore they are hidden in the errors of the neutron diffraction experiment.

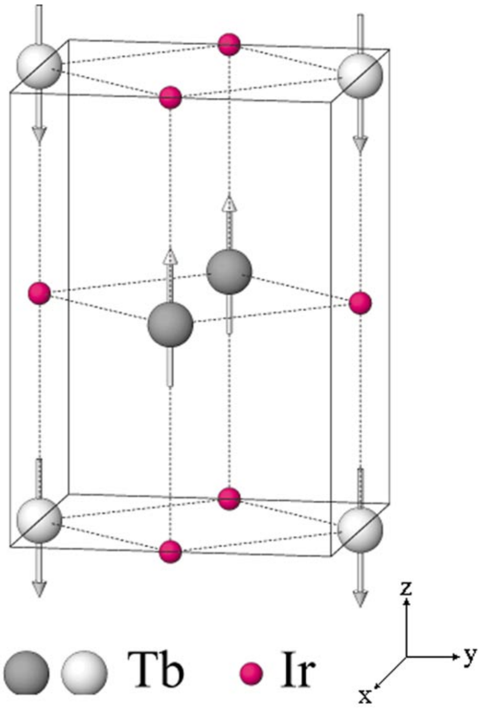

Figure 6. The type I magnetic structure of Sr_2TbIrO_6. Only terbium and iridium ions are depicted.

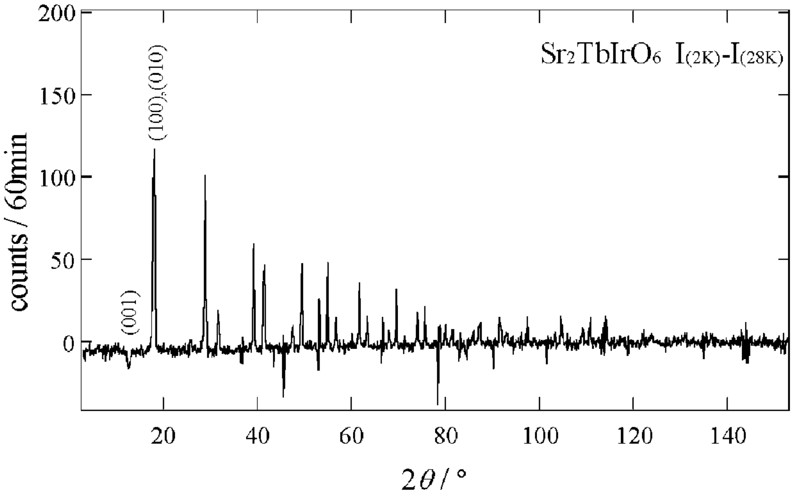

Figure 7. The difference in the intensity of neutron diffraction profiles for Sr_2TbIrO_6 between that at 2 K and at 28 K.

3.2. *Magnetic susceptibility measurement for solid solutions $Sr_2Ce_xTb_{1-x}O_6$*

The temperature dependence of the magnetic susceptibilities for $Sr_2Ce_xTb_{1-x}IrO_6$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.7, . . . , 1.0) was measured under the zero-field-cooled condition (ZFC), and the results are shown in figure 8. Since the magnetic moment of the Ir^{4+} ion is rather smaller than

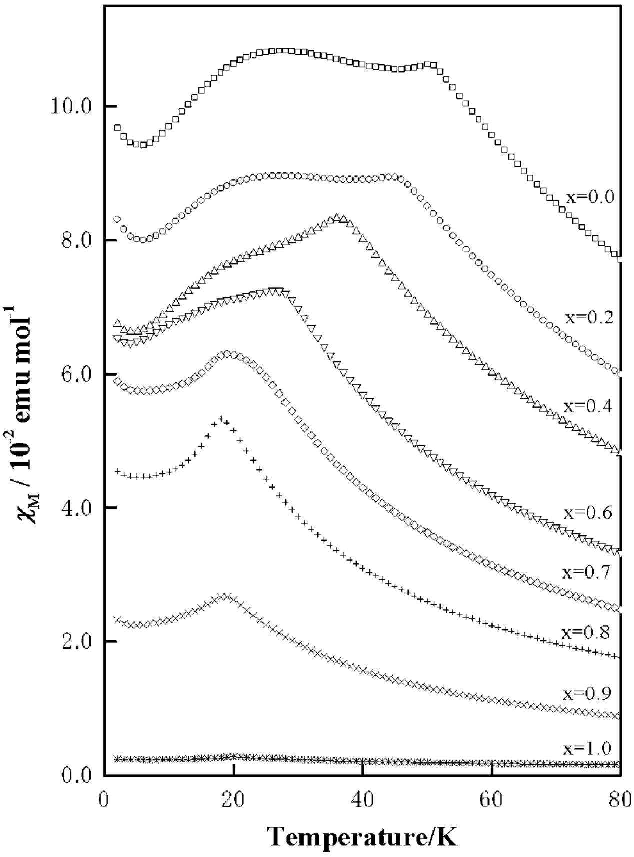

Figure 8. Temperature dependence of the magnetic susceptibilities of $Sr_2Ce_xTb_{1-x}IrO_6$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9, 1.0).

that of the Tb^{4+} ion, the magnetic susceptibilities of $Sr_2Ce_xTb_{1-x}IrO_6$ ($0.0 \leqslant x \leqslant 0.9$) are almost entirely due to the Tb^{4+} ion. As the x value increases (the ratio of Tb^{4+} decreases), the antiferromagnetic transition temperature $T_N = 51$ K (for Sr_2TbIrO_6, $x = 0.0$) decreases and the maximum in the susceptibility–temperature curve becomes broad. The anomaly found at $T_A = 27$ K becomes ambiguous and its temperature decreases with increasing x value. For the compounds with $x \geqslant 0.8$ the anomaly peaks in the susceptibility against temperature disappear.

Now, we will discuss the pathway of the antiferromagnetic interaction found in $Sr_2Ce_xTb_{1-x}IrO_6$. In this case, three kinds of interaction are predicted, (i) the interactions between Tb^{4+} ions along the pathway of nearest neighbours (NN) or next-nearest neighbours (NNN), (ii) the interactions between Tb^{4+} and Ir^{4+} along the pathway of Tb–O–Ir and (iii) the interactions between Ir^{4+} ions along the pathway of nearest neighbours or next-nearest neighbours. Experimental results that the antiferromagnetic transition temperature (T_N) for $Sr_2Ce_xTb_{1-x}IrO_6$ decreases greatly with decreasing ratio of Tb^{4+}, and the temperature of the anomaly in the magnetic susceptibility at $T_A = 27$ K is relatively insensitive to decreasing of the ratio of Tb^{4+} ions indicate that the pathway of magnetic interactions at $T_N = 51$ K must involve Tb^{4+} ions, i.e. (i) or (ii).

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