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Magnetic and neutron diffraction study on ordered perovskites Sr_2LnRuO_6 (Ln=Tb, Ho)

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Abstract

Magnetic properties of ordered perovskite-type compounds Sr_2LnRuO_6 (Ln=Tb, Ho) are reported. Powder neutron diffraction measurements at 10 K, 25 K and room temperature were performed to investigate their crystal and magnetic structures. Both of these compounds are distorted perovskites with space group $P2_1/n$ and a 1:1 ordered arrangement of Ln^{3+} and Ru^{5+} over the six-coordinate sites. Data collected at 10 K and 25 K show that they have a long range antiferromagnetic ordering involving both Ln^{3+} and Ru^{5+}. Each of these ions orders in a Type I arrangement. The direction of the magnetic moments is along the *c*-axis for Sr_2HoRuO_6, while it is canted by ca. 20° from the *c*-axis for Sr_2TbRuO_6. The magnetic susceptibility and specific heat measurements show the existence of magnetic transitions at 41 K for Sr_2TbRuO_6 and at 36 K for Sr_2HoRuO_6. The field-dependence of the magnetization was measured and a small hysteresis loop was found below magnetic transition temperatures, indicating the existence of a weak ferromagnetic moment associated with the antiferromagnetism. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ordered perovskite-type oxides A_2LnMO_6 (A=alkaline-earth elements; Ln=lanthanide elements; M=4d or 5d transition elements) in which the Ln and M elements regularly order, show a variety of magnetic behavior at low temperatures.

We have been greatly interested in the compounds containing ruthenium ions. The electronic structure of Ru^{5+} is $[Kr]4d^3$ ([Kr]: krypton core). Such highly oxidized cations from the second transition series sometimes show quite unusual magnetic behavior.

Recently, we synthesized the perovskites Sr_2LnRuO_6 (Ln=Eu~Lu) and investigated their magnetic properties [1]. They have the ordered perovskite-type structure and they become monoclinically distorted with the increase of ionic Ln^{3+} radius. These compounds show magnetic transition at 30~46 K and the complicated temperature-dependence of magnetic susceptibilities below the transition temperatures. Furthermore, small magnetic hysteresis loops have been found at low temperatures. We have come to a conclusion that magnetic transitions found in the perovskites Sr_2LnRuO_6 are antiferromagnetic and that the weak ferromagnetic moments associated with the antiferromagnetism are also present.

In order to explain the complicated temperature-dependence of magnetic susceptibilities for Sr_2LnRuO_6 (Ln=Eu~Lu), we have performed powder neutron diffraction, magnetic susceptibility, magnetization, and specific heat measurements in detail. In this paper, we will report the crystal and magnetic structures and magnetic properties of both Sr_2TbRuO_6 [2] and Sr_2HoRuO_6 [3].

2. Experimental

Polycrystalline samples of Sr_2TbRuO_6 and Sr_2HoRuO_6 were prepared by firing the appropriate amounts of $SrCO_3$, Tb_4O_7 or Ho_2O_3, and RuO_2, first at 900°C for 12 h and then 1200°C for 60 h in air with several interval regular grinding and pelleting. The progress of the reactions were monitored by powder X-ray diffraction measurements.

Powder neutron diffraction profiles were measured at 10 K, 25 K and room temperature using a high-resolution powder diffractometer (HRPD) at the JRR-3M reactor (Japan Atomic Energy Research Institute) [4], with a Ge (331) monochromator ($\lambda=1.8230$ Å) at both 10 K and 25 K and with a Si (533) monochromator ($\lambda=1.1624$ Å) at

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room temperature for Sr_2HoRuO_6. For Sr_2TbRuO_6, measurements were performed at 10 K and room temperature with the Ge (331) monochromator. The collimators used were 6′–20′–6′, which were placed before and after the monochromator, and between the sample and each detector. The set of 64 detectors and collimators, which were placed every 2.5 degrees, rotate around the sample. Crystal and magnetic structures were determined by the Rietveld technique, using program RIETAN94 [5].

The field-dependence of the magnetization was measured at several temperatures over the applied magnetic field range $-5T<H<5T$, and the temperature-dependence of the DC magnetic susceptibility was recorded in an applied field of 0.1T over the temperature range $5\ K<T<300\ K$, using a SQUID magnetometer (Quantum Design, MPMS5S). The magnetization (at 5 K and 25 K) and all the susceptibility measurements were performed under two sets of conditions, i.e. after zero field cooling (ZFC) and after field cooling (FC).

Specific heat measurements were performed for both compounds, using a relaxation technique with a commercial heat capacity measuring system (Quantum Design, PPMS) in the temperature range 2~100 K. The sample in the form of pellet was mounted on a thin aluminum plate with apiezon grease for better thermal contact.

3. Results and discussion

3.1. Crystal structure

Both compounds were found to crystallize in a single phase by the X-ray diffraction measurements. The Rietveld analysis for the neutron diffraction data shows that the crystal structures of Sr_2TbRuO_6 and Sr_2HoRuO_6 were both a monoclinic perovskite with the space group $P2_1/n$ (No.14) and had an ordered arrangement between Ru^{5+} and Tb^{3+} (or Ho^{3+}) over the six-coordinate B sites of the perovskite ABO_3. The crystallographic data at room temperature determined for these compounds are listed in Table 1 for Sr_2HoRuO_6 and Table 2 for Sr_2TbRuO_6. The unit cell is related to the primitive perovskite unit cell (a_p) by $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$. The crystal structure of Sr_2TbRuO_6 is illustrated in Fig. 1.

Table 1
Crystallographic data for Sr_2HoRuO_6 at room temperature

Atom	Site	x	y	z	$B/Å^2$
Space group $P2_1/n$					
$a=5.7710(3)$ Å		$b=5.7801(3)$ Å	$c=8.1640(4)$ Å	$\beta=90.200(3)°$	
$R_{wp}=$ 10.00%		$R_I=2.95\%$	$R_F=1.35\%$	$R_e=7.30\%$.	
Sr	4e	0.0053(13)	0.0281(5)	0.2479(11)	0.79(4)
Ho	2d	1/2	0	0	0.13(5)
Ru	2c	1/2	0	1/2	0.48(6)
O(1)	4e	0.2663(11)	0.2966(13)	0.0357(9)	0.92(9)
O(2)	4e	0.2010(11)	−0.2280(12)	0.0354(8)	0.74(8)
O(3)	4e	−0.0642(11)	0.4852(10)	0.2334(8)	0.83(7)

Table 2
Crystallographic data for Sr_2TbRuO_6 at room temperature

Atom	Site	x	y	z	$B/Å^2$
Space group $P2_1/n$					
$a=5.7932(2)$ Å		$b=5.8107(1)$ Å	$c=8.2011(3)$ Å	$\beta=90.249(2)°$	
$R_{wp}=6.26\%$		$R_I=1.96\%$	$R_F=1.39\%$	$R_e=5.54\%$.	
Sr	4e	0.0071(11)	0.0291(5)	0.2488(8)	0.8(1)
Tb	2d	1/2	0	0	0.3(1)
Ru	2c	1/2	0	1/2	0.3(1)
O(1)	4e	0.2683(8)	0.2988(9)	0.0360(7)	0.5(1)
O(2)	4e	0.1967(9)	−0.2301(9)	0.0387(6)	0.8(1)
O(3)	4e	−0.0696(8)	0.4847(8)	0.2332(6)	0.9(1)

3.2. Magnetic properties

3.2.1. Sr_2HoRuO_6

The temperature-dependence of the magnetic susceptibilities and specific heat for Sr_2HoRuO_6 is shown in Fig. 2(a). It is found that the divergence in the magnetic susceptibilities between the FC and ZFC occurs at 36 K and that the maximum of susceptibilities appears at 15 K (for FC) and 20 K (for ZFC). The specific heat measurements show a λ-type anomaly at 36 K and a broad anomaly at 11 K. We consider that the divergence between the FC and ZFC susceptibilities indicates the presence of a ferromagnetic moment or a spin-glass. In order to study the origin of the divergence between FC and ZFC susceptibilities, the field-dependence of the magnetization was measured at various temperatures (5~100 K), and the

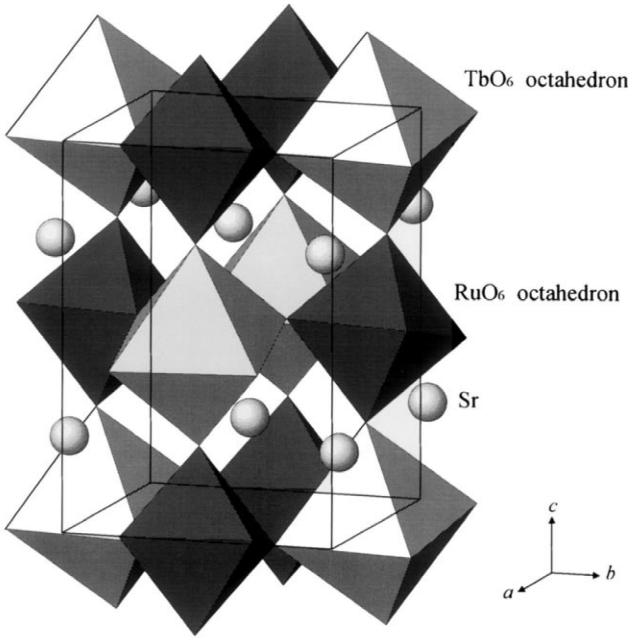

Fig. 1. The crystal structure of Sr_2TbRuO_6.

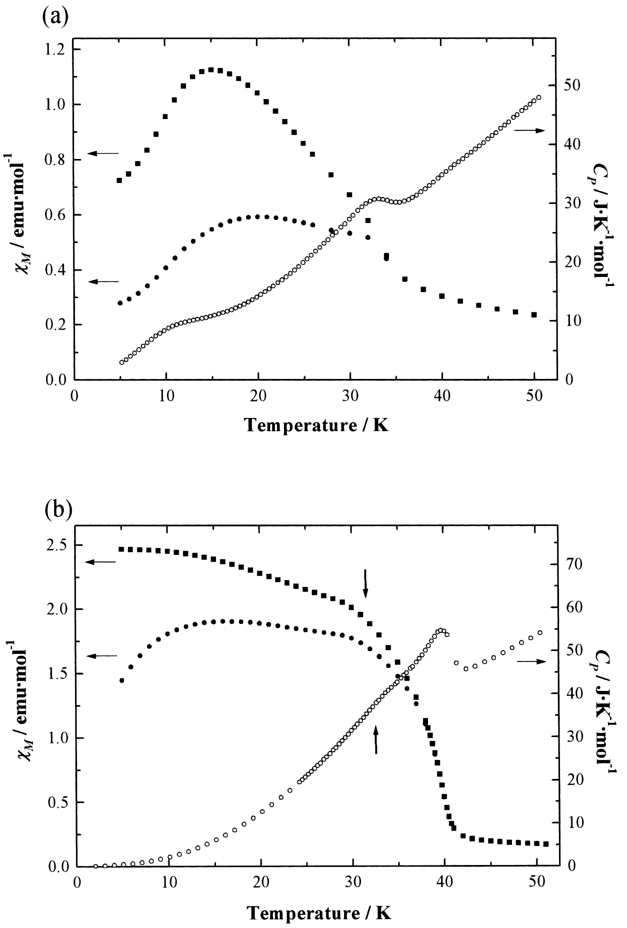

Fig. 2. Temperature dependence of the specific heat (○) and the ZFC (●) and FC (■) magnetic susceptibilities. (a): Sr_2HoRuO_6, (b): Sr_2TbRuO_6.

magnetization measurements under field-cooled conditions were also performed at 5 K and 25 K. It was observed that the FC and ZFC hysteresis curves are the same. This agreement indicates the absence of a spin glass phase. If a spin glass transition occurred, the FC magnetization should be larger than the ZFC magnetization because of the freezing of the induced moment. We found a small magnetic hysteresis loop at 5~30 K, indicating a ferromagnetic moment in Sr_2HoRuO_6 calculated to be 0.04~0.13 μ_B/mol at 5~30 K. For compounds with low crystal symmetry such as monoclinic, a Dzyaloshinsky–Moriya (D–M) interaction can exist between the ordered elements, which results in the existence of a weak ferromagnetic moment associated with the antiferromagnetism.

3.2.2. Sr_2TbRuO_6

The magnetic susceptibilities and specific heat capacities of Sr_2TbRuO_6 are plotted as a function of temperature in Fig. 2(b). The magnetic susceptibility data show that a magnetic transition occurs at 41 K. The specific heat measurements show a λ-type anomaly at 41 K. Magnetic hysteresis measurements at 36 K indicate the existence of a small hysteresis, and the remanent magnetization is estimated to be about 0.15 μ_B from the magnetic hysteresis curve. These results indicate that the magnetic transition observed at 41 K is an antiferromagnetic transition rather than a ferromagnetic one, and that the small remanent magnetization and the divergence between the FC and ZFC susceptibilities are derived from the weak ferromagnetic moment associated with this antiferromagnetism.

In addition, another broad peak may be observed at 32 K in the specific heat vs. temperature curve. An anomaly of the magnetic susceptibility was also observed at 31 K. However, the magnetic hysteresis curves measured around this temperature are very similar except for the difference in the remanent magnetization (0.15 μ_B at 36 K, 0.26 μ_B at 25 K). This magnetic transition may be a reorientation of the magnetic moments [6].

3.3. Magnetic structures

Neutron diffraction measurements at 10 K and 25 K for Sr_2HoRuO_6 and at 10 K for Sr_2TbRuO_6 show that a number of low-angle peaks, which are not observed at room temperature, appear in their diffraction profiles, indicating the presence of an antiferromagnetic ordering. The neutron diffraction profile for Sr_2TbRuO_6 at 10 K is shown in Fig. 3.

3.3.1. Sr_2HoRuO_6

Large (010) and (100) peaks ($2\theta \approx 18.2°$) are observed in the profiles of Sr_2HoRuO_6 at 10 K and 25 K, but the (001) peak ($2\theta \approx 12.8°$) is not found. This fact indicates that the alignment of the magnetic moments of Sr_2HoRuO_6 is in the *c* direction. We have performed the Rietveld analysis on the assumption that all the magnetic moments are collinear. The magnetic structure of Sr_2HoRuO_6 is illustrated in Fig. 4. In this magnetic structure, both the magnetic moments of Ho^{3+} and Ru^{5+} ions are ordered antiferromagnetically. Each of the ions orders in a Type I arrangement. In the ab plane, the magnetic moments of Ho^{3+} and Ru^{5+} ions are coupled ferrimagnetically. The ordered magnetic moments are 2.74(9) μ_B for Ru^{5+} and 6.66(8) μ_B for Ho^{3+} at 10 K, and 2.19(10) μ_B for Ru^{5+} and 3.02(7) μ_B for Ho^{3+} at 25 K. This result means that the ordered magnetic moments of lanthanide ions increase with decreasing temperature. The values of the ordered moments for Ru^{5+} are larger than those of other perovskite compounds containing Ru^{5+} [7–11]. This may be attributable to the fact that the ordered magnetic moment of Ru^{5+} is estimated to be larger because of the similarity in the magnetic peak positions between Ru^{5+} and Ho^{3+}. Since the weak ferromagnetic components observed in the magnetization measurements are very small, we cannot estimate the magnitude of the moments from this refinement of neutron diffraction profiles.

In addition to the magnetic anomaly at 36 K (Néel temperature), the magnetic susceptibilities show a maxi-

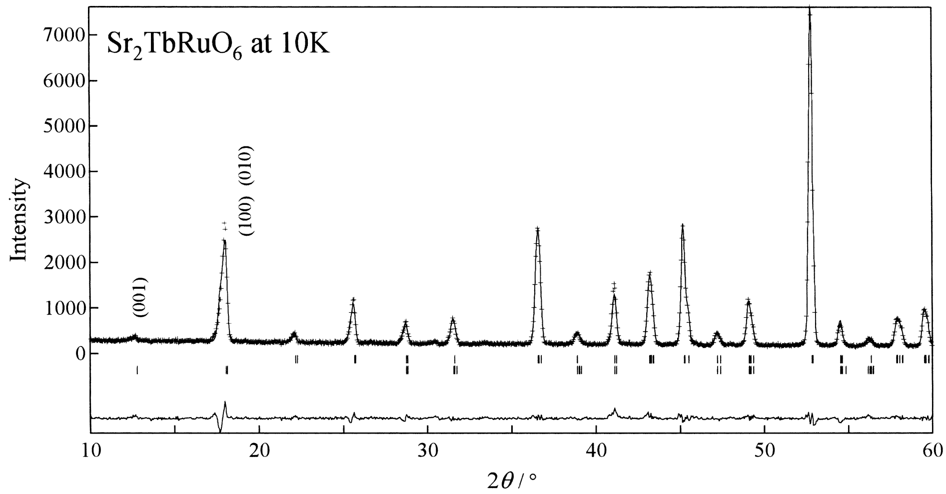

Fig. 3. Powder neutron diffraction profile for Sr_2TbRuO_6 at 10 K. The nuclear reflection positions are shown as upper vertical marks and magnetic ones are shown as lower vertical marks.

mum at 15 K for FC and at 20 K for ZFC and the specific heat show an anomaly at 11 K. The neutron diffraction profile measured at 25 K and resulting calculations indicate that there is a long range antiferromagnetic ordering even at this temperature. The only difference between the 10 K and 25 K data is in the intensity of the magnetic Bragg peaks, i.e. the peaks at 10 K are more intense than those at 25 K. The origin of these magnetic anomalies may be a reorientation of the magnetic moments.

3.3.2. Sr_2TbRuO_6

A number of magnetic reflection peaks are also observed in the diffraction profile of Sr_2TbRuO_6 measured at 10 K. The positions of their peaks very closely resemble those for Sr_2HoRuO_6 measured at 10 K, except for the difference in the intensity of the (001) peak ($2\theta \approx 12.8°$). In the case of Sr_2HoRuO_6, this magnetic peak was negligibly weak, indicating that the alignment of the magnetic moments was parallel to the *c* direction. On the other hand, the corresponding (001) peak observed for the present Sr_2TbRuO_6 has significant intensity. We refined the magnetic structure of Sr_2TbRuO_6 using a model in which Sr_2TbRuO_6 has the same magnetic structure as Sr_2HoRuO_6 and the alignment of the magnetic moments cants from the *c*-axis to some extent.

Very good agreement between the observed data and calculated intensities was obtained. The magnetic structure of Sr_2TbRuO_6 is quite similar to that of Sr_2HoRuO_6, i.e. the magnetic moments of both Tb^{3+} and Ru^{5+} ions are ordered antiferromagnetically, and each of these orders on a type I arrangement. For Sr_2TbRuO_6, the gradient of the magnetic moments against the *c*-axis is about 20°. The ordered magnetic moments at 10 K are 2.99(11) μ_B for Ru^{5+} and 4.98(12) μ_B for Tb^{3+}.

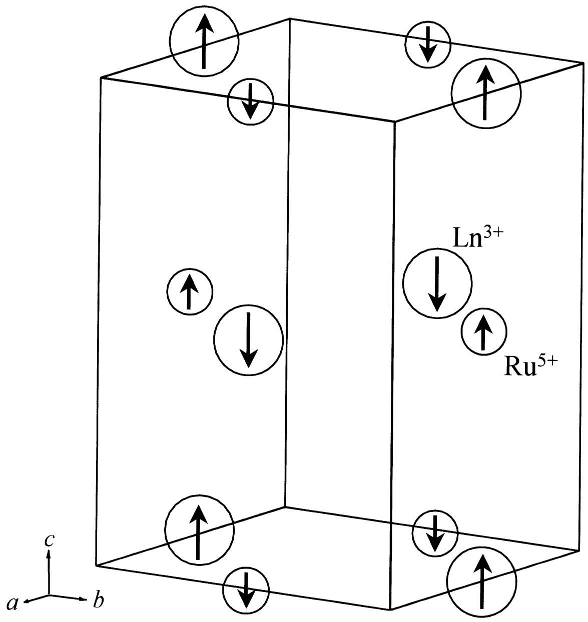

Fig. 4. The magnetic structure of Sr_2LnRuO_6 (Ln=Tb, Ho). Diamagnetic ions are omitted. Larger circles Ln^{3+}; smaller circles Ru^{5+}. For the case of Sr_2TbRuO_6, the direction of the magnetic moments cants by about 20° against the *c*-axis.

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