

Magnetic Properties of $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Tb}, \text{Ho}$)

Yoshihiro DOI, Yukio HINATSU, Ken-ichi OIKAWA¹, Yutaka SHIMOJO¹ and Yukio MORII¹

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan
¹*Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-1195, Japan*

Magnetic properties of ordered perovskite-type compounds $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Tb}, \text{Ho}$) have been investigated. The magnetization and specific heat measurements show the existence of magnetic transitions at 41 K for $\text{Sr}_2\text{TbRuO}_6$ and at 36 K for $\text{Sr}_2\text{HoRuO}_6$. Powder neutron diffraction measurements were performed for $\text{Sr}_2\text{TbRuO}_6$ at 10 K and room temperature, and for $\text{Sr}_2\text{HoRuO}_6$ at 10 K, 25 K and room temperature. The crystal structure at room temperature is monoclinic with space group $P2_1/n$, and the Ru^{5+} and Ln^{3+} ions are structurally ordered at the B sites of the ABO_3 perovskite-type structure. Data collected at low temperatures show that these compounds have a long range antiferromagnetic ordering involving both Ru^{5+} and Ln^{3+} . Each magnetic moment of these ions orders in a Type I arrangement and they are antiparallel with each other in the ab -plane. The direction of the magnetic moments for $\text{Sr}_2\text{HoRuO}_6$ is along the c axis, while that for $\text{Sr}_2\text{TbRuO}_6$ is canted from the c axis by about 20° . The ordered magnetic moments at 10 K for $\text{Sr}_2\text{TbRuO}_6$ are $3.0(1) \mu_B$ (Ru^{5+}) and $5.0(1) \mu_B$ (Tb^{3+}), and those at 10 K for $\text{Sr}_2\text{HoRuO}_6$ are $2.74(9) \mu_B$ (Ru^{5+}) and $6.66(8) \mu_B$ (Ho^{3+}).

KEYWORDS: ordered perovskite, antiferromagnetism, neutron diffraction, magnetization, specific heat

§1. Introduction

Ordered perovskite-type oxides $A_2\text{LnMO}_6$ ($A =$ alkaline-earth elements; $\text{Ln} =$ 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 $[\text{Kr}]4d^3$ ($[\text{Kr}]$: krypton core). Such highly oxidized cations from the second transition series sometimes show quite unusual magnetic behavior.

Recently, we synthesized the perovskites $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu-Lu}$) and investigated their magnetic properties.¹⁾ They have the ordered perovskite-type structure and 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 MH^{-1} (M : magnetization, H : magnetic field) 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 $\text{Sr}_2\text{LnRuO}_6$ are antiferromagnetic and that the weak ferromagnetic moments associated with the antiferromagnetism are also present.

In order to explain the complicated temperature-dependence of MH^{-1} for $\text{Sr}_2\text{LnRuO}_6$, we have performed the powder neutron diffraction, MH^{-1} , magnetization, and specific heat measurements in detail. In this paper, we will report the crystal and magnetic structures and magnetic properties of both $\text{Sr}_2\text{TbRuO}_6$ ²⁾ and $\text{Sr}_2\text{HoRuO}_6$.³⁾

§2. Experimental

Polycrystalline samples of $\text{Sr}_2\text{TbRuO}_6$ and $\text{Sr}_2\text{HoRuO}_6$ 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 hours and then 1200°C for 60 hours 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 ($\lambda = 1.8230\text{\AA}$) at both 10 and 25 K and with a Si (533) monochromator ($\lambda = 1.1624\text{\AA}$) at room temperature for $\text{Sr}_2\text{HoRuO}_6$. For $\text{Sr}_2\text{TbRuO}_6$, 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 RIETAN94⁵⁾ (local version). We assume that all the magnetic moments are collinear.

The field-dependence of the magnetization was measured at several temperatures over the applied magnetic field range $-5\text{T} < H < 5\text{T}$, and the temperature-dependence of MH^{-1} was recorded in an applied field of 0.1T over the temperature range $5\text{K} < T < 300\text{K}$, using a SQUID magnetometer (Quantum Design, MPMS-5S). The magnetization (at 5 K and 25 K) and all the magnetic 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 the compounds, using a relaxation technique with a commercial heat capacity measuring system (Quantum Design, PPMS) in the temperature range 5-100 K.

§3. Results and Discussion

3.1 Crystal structure

Both the 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 $\text{Sr}_2\text{TbRuO}_6$ and $\text{Sr}_2\text{HoRuO}_6$ were both a monoclinic perovskite with the space group $P2_1/n$ 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 I for $\text{Sr}_2\text{HoRuO}_6$ and Table II for $\text{Sr}_2\text{TbRuO}_6$. 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 $\text{Sr}_2\text{TbRuO}_6$ is illustrated in Fig.1.

Table I. Crystallographic data for $\text{Sr}_2\text{HoRuO}_6$ at room temperature.

Atom	Site	x	y	z	$B(\text{\AA}^2)$
Sr	4e	0.0053(13)	0.0281(5)	0.2479(11)	0.8(1)
Ho	2d	1/2	0	0	0.1(1)
Ru	2c	1/2	0	1/2	0.5(1)
O(1)	4e	0.2663(11)	0.2966(13)	0.0357(9)	0.9(1)
O(2)	4e	0.2010(11)	-0.2280(12)	0.0354(8)	0.7(1)
O(3)	4e	-0.0642(11)	0.4852(10)	0.2334(8)	0.8(1)

Note: $a = 5.7710(3)\text{\AA}$, $b = 5.7801(3)\text{\AA}$, $c = 8.1640(4)\text{\AA}$, $\beta = 90.200(3)^\circ$, $R_{\text{wp}} = 10.00\%$, $R_{\text{I}} = 2.95\%$, $R_{\text{F}} = 1.35\%$, $R_{\text{e}} = 7.30\%$.

Table II. Crystallographic data for $\text{Sr}_2\text{TbRuO}_6$ at room temperature.

Atom	Site	x	y	z	$B(\text{\AA}^2)$
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(8)	0.0387(6)	0.8(1)
O(3)	4e	-0.0696(8)	0.4847(8)	0.2332(6)	0.9(1)

Note: $a = 5.7932(2)\text{\AA}$, $b = 5.8107(1)\text{\AA}$, $c = 8.2011(3)\text{\AA}$, $\beta = 90.249(2)^\circ$, $R_{\text{wp}} = 6.26\%$, $R_{\text{I}} = 1.96\%$, $R_{\text{F}} = 1.39\%$, $R_{\text{e}} = 5.54\%$.

3.2 Magnetic properties

The temperature-dependence of MH^{-1} and specific heat capacities for $\text{Sr}_2\text{HoRuO}_6$ is shown in Fig.2(a). It is found that the divergence in the MH^{-1} between the FC and ZFC occurs at 36 K. The specific heat measurements show a λ -type anomaly at 36 K. We consider that this divergence indicates the presence of a ferromagnetic moment or a spin-glass transition. In order to study the origin of the divergence between FC and ZFC MH^{-1} curves, the field-dependence of the magnetization were measured at 5 K and 25 K under the FC and ZFC conditions. It was observed that the FC and ZFC hysteresis curves are the same. This agreement indicates the ab-

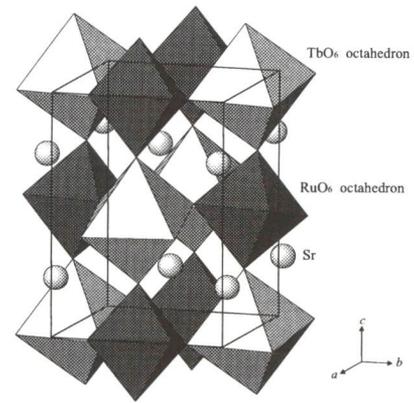


Fig.1. The crystal structure of $\text{Sr}_2\text{TbRuO}_6$.

sence of a spin glass phase. For compounds with a 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. In addition, the maximum of MH^{-1} appears at 15 K (for FC) and 20 K (for ZFC). A broad peak of the specific heat is observed at about 11 K.

The MH^{-1} and specific heat capacities of $\text{Sr}_2\text{TbRuO}_6$ are plotted as a function of temperature in Fig.2(b). The MH^{-1} curves 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 show the existence of a small hysteresis, and the remanent magnetization is estimated to be about $0.15 \mu_B$ 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 MH^{-1} curves 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 MH^{-1} was also observed at 31 K. However, the magnetic hysteresis curves measured at 36 K and 25 K are very similar except for the difference in the remanent magnetization ($0.15 \mu_B$ at 36 K and $0.26 \mu_B$ at 25 K). This magnetic anomaly may be a reorientation of the magnetic moments.⁶⁾

3.3 Magnetic structures

Neutron diffraction measurements at 10 K and 25 K for $\text{Sr}_2\text{HoRuO}_6$ and at 10 K for $\text{Sr}_2\text{TbRuO}_6$ are 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 profiles at 10 K are shown in Fig.3.

Large (010) and (100) peaks ($2\theta \sim 18.2^\circ$) are observed in the profiles of $\text{Sr}_2\text{HoRuO}_6$ at 10 K and 25 K, but the (001) peak ($2\theta \sim 12.8^\circ$) is not found. This fact indicates that the alignment of the magnetic moments of $\text{Sr}_2\text{HoRuO}_6$ is in the c direction. The magnetic structure of $\text{Sr}_2\text{HoRuO}_6$ is illustrated in Fig.4. In this magnetic

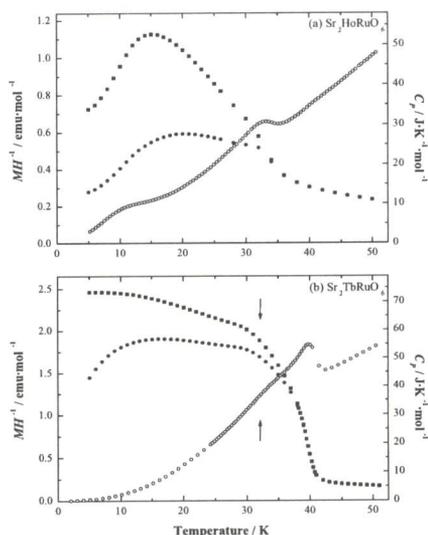


Fig. 2. Temperature dependence of the specific heat (hollow circle) and the ZFC (filled circle) and FC (filled square) MH^{-1} . (a): $\text{Sr}_2\text{HoRuO}_6$, (b): $\text{Sr}_2\text{TbRuO}_6$. Two vertical arrows at 32 K and 31 K show specific heat anomaly and MH^{-1} one, respectively.

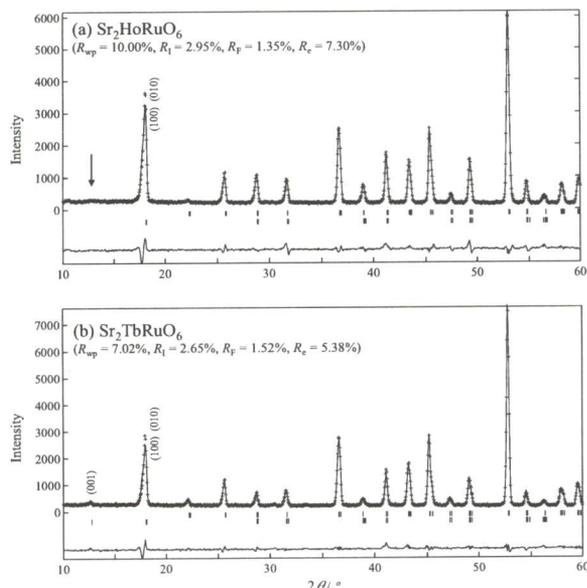


Fig. 3. Powder neutron diffraction profiles for $\text{Sr}_2\text{HoRuO}_6$ (a) and for $\text{Sr}_2\text{TbRuO}_6$ (b) at 10 K. The nuclear reflection positions are shown as upper vertical marks and magnetic ones are shown as lower vertical marks. A vertical arrow shows a expected (001) peak position for $\text{Sr}_2\text{HoRuO}_6$.

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 $2.74(9) \mu_B$ for Ru^{5+} and $6.66(8) \mu_B$ for Ho^{3+} at 10 K, and $2.2(1) \mu_B$ for Ru^{5+} and $3.02(7) \mu_B$ for Ho^{3+} at 25 K. This result means that the ordered magnetic moments of Ho^{3+} increase with decreasing temperature. The values of the ordered moments for Ru^{5+} are larger than those of other perovskite compounds containing Ru^{5+} .⁷⁻⁹⁾

In addition to the magnetic anomaly at 36 K (Néel temperature), the MH^{-1} of $\text{Sr}_2\text{HoRuO}_6$ show a maximum at 15 K for FC and at 20 K for ZFC. The neutron

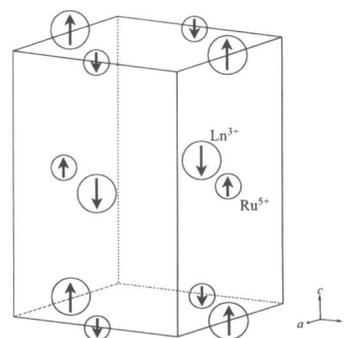


Fig. 4. The magnetic structure of $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Tb}, \text{Ho}$). Diamagnetic ions are omitted. Larger circles Ln^{3+} ; smaller circles Ru^{5+} . For the case of $\text{Sr}_2\text{TbRuO}_6$, the direction of the magnetic moments cants by about 20° against the c axis.

diffraction profile measured at 25 K and resulting calculations indicate that there is a magnetic 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. However, the origin of the magnetic anomaly at 15-20 K is not clear at present.

A number of magnetic reflection peaks are also observed in the diffraction profile of $\text{Sr}_2\text{TbRuO}_6$ measured at 10 K. The positions of their peaks very closely resemble those for $\text{Sr}_2\text{HoRuO}_6$ measured at 10 K, except for the difference in the intensity of the (001) peak ($2\theta \sim 12.8^\circ$). In the case of $\text{Sr}_2\text{HoRuO}_6$, this magnetic peak was negligibly weak, indicating that the alignment of the magnetic moments is parallel to the c direction. On the other hand, the corresponding (001) peak observed for the present $\text{Sr}_2\text{TbRuO}_6$ has significant intensity. We refined the magnetic structure of $\text{Sr}_2\text{TbRuO}_6$ using a model in which $\text{Sr}_2\text{TbRuO}_6$ has the same magnetic structure as $\text{Sr}_2\text{HoRuO}_6$ 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 $\text{Sr}_2\text{TbRuO}_6$ is quite similar to that of $\text{Sr}_2\text{HoRuO}_6$. The gradient of the magnetic moments against the c axis is about 20° . The ordered magnetic moments at 10 K are $3.0(1) \mu_B$ for Ru^{5+} and $5.0(1) \mu_B$ for Tb^{3+} .

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