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Magnetic and neutron diffraction study on the ordered perovskite Sr_2HoRuO_6

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Magnetic properties of an ordered perovskite compound Sr_2HoRuO_6 have been reported. Powder neutron diffraction measurements at 10 K, 25 K and room temperature were performed to investigate the crystal and magnetic structures of Sr_2HoRuO_6. As a result of the refinement of the data collected at room temperature, it was found that the crystal structure of this compound is a distorted perovskite [$a = 5.7710(3)$ Å, $b = 5.7801(3)$ Å, $c = 8.1640(4)$ Å and $\beta = 90.200(3)^\circ$] with space group $P2_1/n$ and a 1 : 1 ordered arrangement of Ru^{5+} and Ho^{3+} over the six-coordinate B sites. Data collected at 10 and 25 K show that Sr_2HoRuO_6 has a long range antiferromagnetic ordering involving both Ru^{5+} and Ho^{3+}. The direction of the magnetic moments is along the *c*-axis. Each of these orders in a type I arrangement and these magnetic moments are antiparallel in the *ab*-plane with each other. Magnetic susceptibility measurements from 5 to 300 K showed the existence of a magnetic transition at 36 K and divergence between zero-field and field cooled conditions below this temperature. The field-dependence of the magnetization was measured and a small magnetic hysteresis loop was found below the divergence temperature indicating the existence of a weak ferromagnetic moment associated with the antiferromagnetism.

1 Introduction

In recent years, the solid-state chemistry of mixed-metal oxides containing platinum group metals has attracted a great deal of interest. These materials adopt a diverse range of structures and show a wide range of electronic properties. We have focused our attention on the structural chemistry and magnetic properties of ordered perovskite-type oxides A_2LnMO_6 (A = Sr, Ba; Ln = lanthanide element; M = 4d or 5d transition element), in which the Ln and M ions regularly order. These oxides show a variety of magnetic behaviors at low temperatures. Recently, we synthesized and investigated the perovskites Sr_2LnRuO_6 (Ln = Eu–Lu).[1] These compounds have the ordered perovskite-type structure and they become monoclinically distorted with an increase of ionic Ln^{3+} radius. These compounds show a magnetic transition at 30–46 K and a complicated temperature dependence of magnetic susceptibilities below the transition temperatures. Furthermore, small magnetic hysteresis loops have been observed at low temperatures. We have come to the conclusion that magnetic transitions found in the perovskites Sr_2LnRuO_6 are antiferromagnetic and that weak ferromagnetic moments associated with the antiferromagnetism are also present. Battle *et al.* reported that Sr_2YRuO_6 and Sr_2LuRuO_6 are antiferromagnetic below 26 and 30 K, respectively, and Sr_2ErRuO_6 shows antiferromagnetic ordering involving both Ru^{5+} and Er^{3+} at *ca.* 40 K according to neutron diffraction.[2–4] Harada *et al.* showed that Sr_2CeIrO_6 and Sr_2TbIrO_6 are antiferromagnetic below 21 and 51 K, respectively.[5] In these A_2LnMO_6 compounds, the magnetic interactions between M ions are important, and furthermore, the magnetic interactions between M and Ln ions also contribute to their antiferromagnetic interactions. In order to explain the complicated temperature dependence of the magnetic susceptibilities for Sr_2LnRuO_6 (Ln = Eu–Lu), we have performed powder neutron diffraction, magnetic susceptibility and magnetization measurements in detail.

Here, we will report the crystal and magnetic structures and magnetic properties of Sr_2HoRuO_6, which has two magnetic transitions (*ca.* 20 and 36 K). Through magnetic measurements, we expect to clarify the magnetic behavior of Sr_2HoRuO_6 in each of three temperature regions (below 20 K, 20–36 K and above 36 K).

2 Experimental

A polycrystalline sample of Sr_2HoRuO_6 was prepared by firing the appropriate amounts of $SrCO_3$, Ho_2O_3 and RuO_2, first at

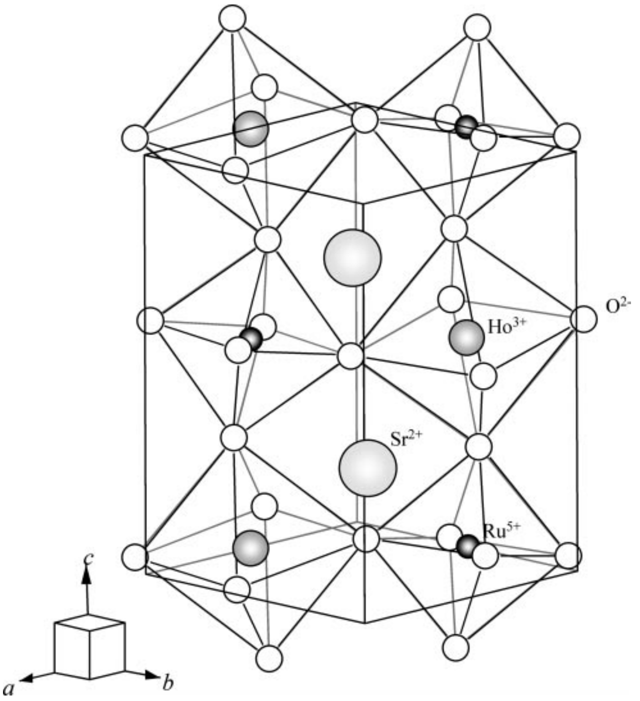

Fig. 1 The crystal structure of Sr_2HoRuO_6.

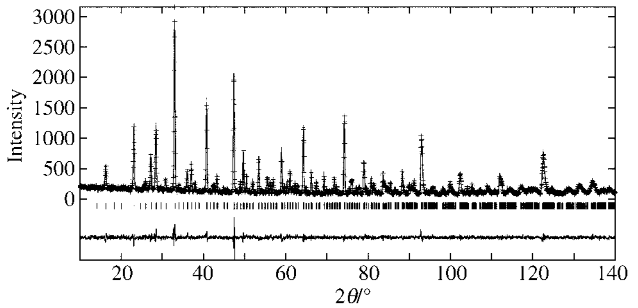

Fig. 2 Powder neutron diffraction profiles for Sr_2HoRuO_6 at room temperature. The calculated and observed profiles are shown by the top solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between the calculated and observed intensities.

1173 °C for 12 h and then 1473 °C for 60 h in air with interval regular grinding and pelleting. The progress of the reactions was monitored by powder X-ray diffraction measurements.

Powder neutron diffraction profiles were measured at 10, 25 K and room temperature using a high-resolution powder diffractometer (HRPD) in the JRR-3M reactor (Japan Atomic Energy Research Institute), with a Ge(331) monochromator ($\lambda = 1.8230$ Å) at both 10 and 25 K and with a Si(533) monochromator ($\lambda = 1.1624$ Å) at room temperature. 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 at intervals of 2.5°, rotate around the sample. Crystal and magnetic structures were determined by the Rietveld technique, using the program Rietan.[6]

The field-dependence of the magnetization was measured at 2, 5, 10, 15, 20, 25, 30, 40 and 100 K over the applied magnetic field range $-5\ \mathrm{T} < H < 5\ \mathrm{T}$, and the temperature-dependence of the dc magnetic susceptibility was made in an applied field of 0.1 T over the temperature range $5\ \mathrm{K} < T < 300\ \mathrm{K}$, using a SQUID magnetometer (Quantum Design, MPMS5S). The magnetization (at 5 and 25 K) and all the susceptibility measurements were performed either using zero field cooling (ZFC) or field cooling (FC) conditions.

3 Results and discussion

3.1 Crystal structure

It was ascertained that the Sr_2HoRuO_6 prepared in this study crystallized in a single phase by the X-ray diffraction measurement at room temperature. All the neutron diffraction data were analyzed by the Rietveld method. As a result of the structural refinement using data collected at room temperature, it was found that the crystal structure of Sr_2HoRuO_6 was a monoclinic perovskite of space group $P2_1/n$ (no. 14) with an ordered arrangement between Ru^{5+} and Ho^{3+} over the six-coordinate B sites. This unit cell is related to the primitive perovskite unit cell (a_p) by $a \approx \sqrt{2}a_p$, $b \approx \sqrt{2}a_p$, $c \approx 2a_p$. The unit cell parameters were $a = 5.7710(3)$ Å, $b = 5.7801(3)$ Å, $c = 8.1640(4)$ Å and $\beta = 90.200(3)°$ ($R_{wp} = 10.00\%$, $R_I = 2.95\%$ and $R_F = 1.35\%$). The crystal structure of Sr_2HoRuO_6 is illustrated in Fig. 1 while the observed and calculated neutron diffraction profiles are plotted in Fig. 2. The refined structural parameters and the bond lengths and angles, calculated from these structural parameters, are listed in Tables 1 and 2, respectively.

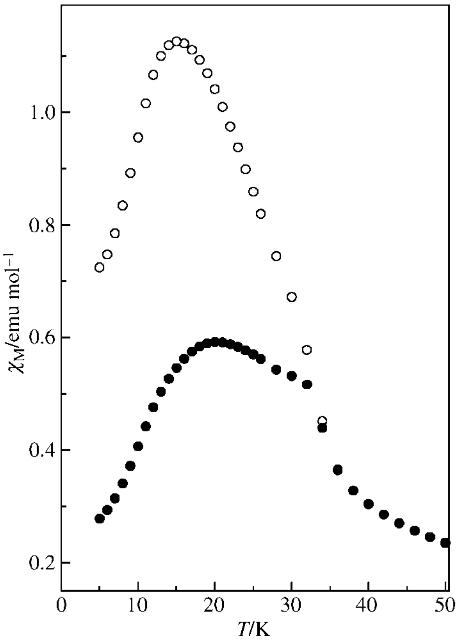

Fig. 3 Temperature-dependence of the ZFC (filled symbols) and FC (open symbols) molar magnetic susceptibilities for Sr_2HoRuO_6 in an applied field of 0.1 T.

3.2 Magnetic properties

The temperature dependence of the magnetic susceptibilities for Sr_2HoRuO_6 is shown in Fig. 3. It is found that the divergence in the magnetic susceptibilities between the FC and ZFC occurs at *ca.* 36 K and that the maximum of the susceptibility appears at *ca.* 15 K (for FC) and *ca.* 20 K (for ZFC). We consider that this divergence indicates the presence of a ferromagnetic moment or a spin-glass transition and that a cusp indicates an antiferromagnetic transition or a spin-glass transition. As will be described below, the possibility of the spin-glass transition is precluded from the results of magnetic hysteresis measurements. The fitting of the Curie–Weiss law to the temperature-dependence of magnetic susceptibilities at higher temperatures ($T > 150$ K) gives an effective magnetic moment (μ_{eff}) and Weiss constant (θ) of 10.6 μ_B and −20 K, respectively. Since the theoretical free-ion magnetic moments of Ru^{5+} and Ho^{3+} are 3.87 and 10.58 μ_B, respectively, the observed effective magnetic moment (μ_{eff}) is lower than the expected value of *ca.* 11.3 μ_B [estimated from $(\mu_{Ru^{5+}}{}^2 + \mu_{Ho^{3+}}{}^2)^{1/2}$] which suggests that the magnetic ions in this compound may be affected by the crystal field to some extent. The negative Weiss constant indicates that the

Table 1 Crystallographic data for Sr_2HoRuO_6 at room temperature from powder neutron profiles

Atom	Site	*x*	*y*	*z*	B/Å^2
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)

$a = 5.7710(3)$ Å, $b = 5.7801(3)$ Å, $c = 8.1640(4)$ Å, $\beta = 90.200(3)°$, $R_{wp} = 10.00\%$, $R_I = 2.95\%$, $R_F = 1.35\%$, $R_e = 7.30\%$.

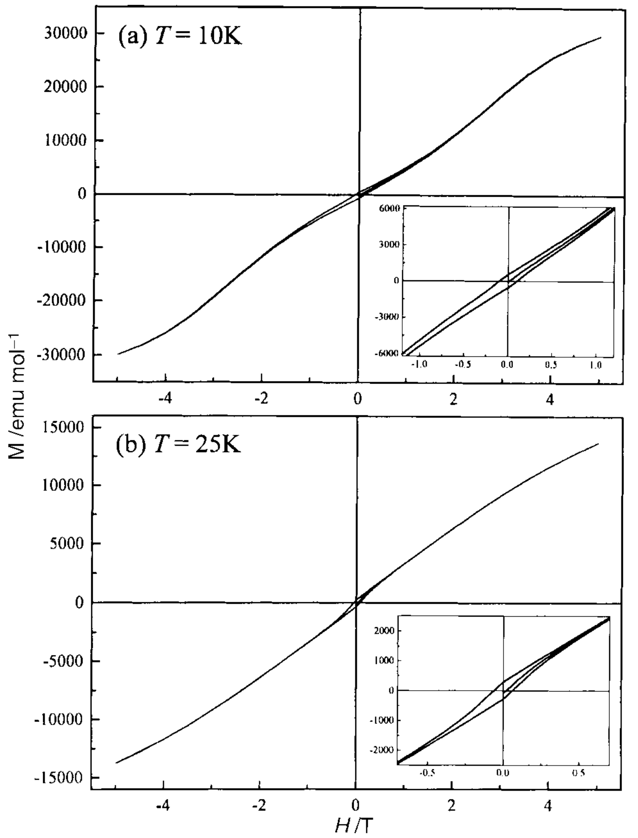

Fig. 4 Field-dependence of the magnetization at 10 K (a) and at 25 K (b).

predominant magnetic interaction in Sr_2HoRuO_6 is antiferromagnetic.

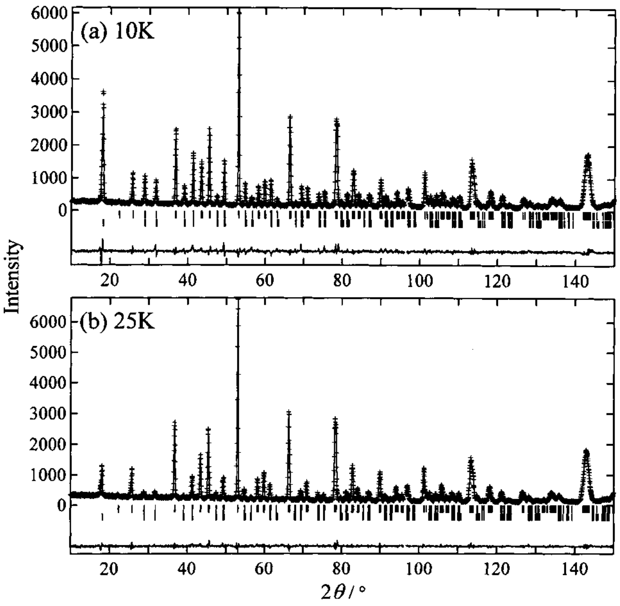

Fig. 5 Powder neutron diffraction profiles for Sr_2HoRuO_6 at 10 K (a) and 25 K (b). The calculated and observed profiles are shown by the top solid line and cross markers, respectively. The nuclear reflection positions are shown as upper vertical marks and magnetic ones by lower vertical marks. The lower trace is a plot of the difference between the calculated and observed intensities.

Table 2 Bond lengths (Å) and bond angles (°) for Sr_2HoRuO_6 at room temperature

Ho–O(1)	2.201(6) × 2	Ru–O(1)	1.956(6) × 2
Ho–O(2)	2.191(7) × 2	Ru–O(2)	1.974(7) × 2
Ho–O(3)	2.208(6) × 2	Ru–O(3)	1.944(6) × 2
Sr–O(1)	2.576(10)	2.774(10)	2.911(11)
Sr–O(2)	2.547(11)	2.823(10)	2.843(10)
Sr–O(3)	2.563(9)	2.675(7)	
O(1)–Ho–O(2)	91.9(3)	O(1)–Ru–O(2)	90.2(4)
O(1)–Ho–O(3)	90.0(2)	O(1)–Ru–O(3)	91.2(4)
O(2)–Ho–O(3)	91.4(3)	O(2)–Ru–O(3)	90.3(3)

In order to study the origin of the divergence between FC and ZFC susceptibilities, the field-dependence of the magnetization were measured at 2, 5, 10, 15, 20, 25, 30, 40 and 100 K, and the magnetization measurements under field-cooled conditions were also performed at 5 and 25 K. The magnetic hysteresis curves measured at 10 and 25 K are shown in Fig. 4 and it is 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 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 0.04–0.125 μ_B mol^{-1} at 5–30 K. 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. Metamagnetic behavior is found below 10 K [see Fig. 4(a)], a temperature lower than the second magnetic transition temperature (15 K for FC; 20 K for ZFC).

3.3 Magnetic structures

Fig. 5 shows the neutron diffraction profiles collected at 10 and 25 K. A number of low-angle peaks, which are not observed at room temperature, appear in these profiles and indicate the presence of an antiferromagnetic ordering. We attempted to determine the magnetic structures by using the magnetic structural data of Sr_2ErRuO_6,[4] but this attempt failed. In that structural model, the magnetic moments were aligned along the *a* axis. Large (010) and (100) peaks ($2\theta \approx 18.2°$) are observed in the profiles of Sr_2HoRuO_6 at 10 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 not in the *a* direction, but rather in the *c* direction. The magnetic structure

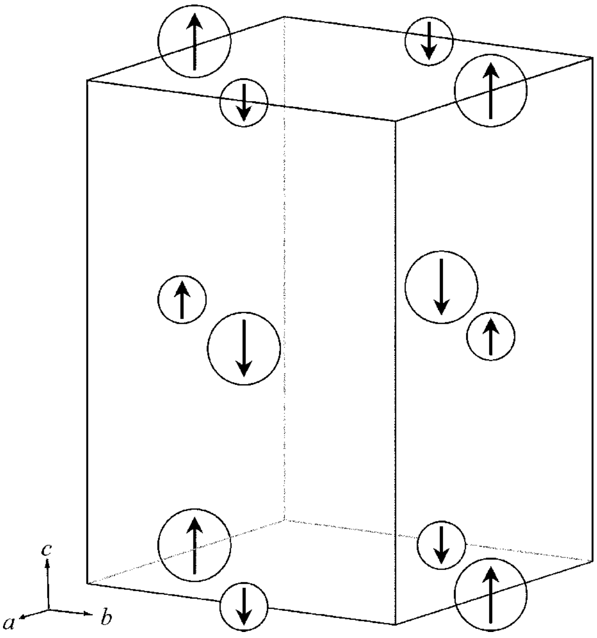

Fig. 6 The magnetic structure of Sr_2HoRuO_6. Diamagnetic ions are omitted. Larger circles Ho^{3+}; smaller circles Ru^{5+}.

Table 3 Crystallographic data for Sr_2HoRuO_6 at 10 and 25 K from powder neutron profiles

Atom	Site	x	y	z	B/Å^2	μ/μ_B
10 K						
$a=5.7628(2)$ Å, $b=5.7841(2)$ Å, $c=8.1468(3)$ Å, $\beta=90.244(2)°$, $R_{wp}=9.24\%$, $R_I=3.20\%$, $R_F=1.80\%$, $R_e=5.41\%$						
Sr	4e	0.0054(17)	0.0327(7)	0.2471(13)	0.20(8)	
Ho	2d	1/2	0	0	0.10(9)	6.66(8)
Ru	2c	1/2	0	1/2	0.58(13)	2.74(9)
O(1)	4e	0.2702(14)	0.3059(14)	0.0308(11)	0.35(15)	
O(2)	4e	0.1966(14)	−0.2250(14)	0.0384(9)	0.11(10)	
O(3)	4e	−0.0696(13)	0.4840(13)	0.2346(9)	0.35(15)	
25 K						
$a=5.7618(2)$ Å, $b=5.7819(1)$ Å, $c=8.1507(2)$ Å, $\beta=90.247(2)°$, $R_{wp}=6.81\%$, $R_I=2.64\%$, $R_F=1.54\%$, $R_e=5.44\%$						
Sr	4e	0.0071(11)	0.0314(5)	0.2485(8)	0.31(6)	
Ho	2d	1/2	0	0	0.13(9)	3.02(7)
Ru	2c	1/2	0	1/2	0.33(9)	2.19(10)
O(1)	4e	0.2673(9)	0.3012(10)	0.0352(7)	0.45(13)	
O(2)	4e	0.1973(9)	−0.2267(10)	0.0375(7)	0.22(11)	
O(3)	4e	−0.0689(9)	0.4828(9)	0.2343(6)	0.38(10)	

of Sr_2HoRuO_6 is illustrated in Fig. 6 and refined structural parameters are listed in Table 3. 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 only difference between the 10 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 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 is in accord with the tendency found for the ordered moments of Sr_2ErRuO_6, *i.e.*, the ordered magnetic moments of lanthanide ions increase with decreasing temperature and do not saturate even at 4.2 K. The values of the ordered moments for Ru^{5+} are larger than those of other perovskite compounds containing Ru^{5+}.[2–4,7,8] 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 compared with the ordered magnetic moments of Ho^{3+} and Ru^{5+} ions, we can not estimate the magnitude of the moments from this refinement of neutron diffraction profiles. From the measurements of the temperature dependence, we have found that the ZFC and FC magnetic susceptibilities begin to diverge below 36 K, and that the ZFC susceptibilities show a maximum at 20 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. We have determined a Néel temperature of Sr_2HoRuO_6 of 36 K. The magnetic susceptibilities show a maximum at 15 K for FC and at 20 K for ZFC, a result that cannot be explained from these measurements. One possibility is that it may be caused by a slight spin flop. In order to elucidate this behavior, further investigations such as specific heat measurements and neutron diffraction measurements using a single crystal sample will be needed.

Acknowledgements

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