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Crystal structures and magnetic properties of ordered perovskites $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu-Lu}$)

Yoshihiro Doi and Yukio Hinatsu

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

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Abstract. The perovskite-type compounds $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu-Lu}$) have been synthesized, and their crystal structures and magnetic properties have been investigated. Powder x-ray diffraction measurements and the Rietveld analysis show that they are monoclinic with space group $P2_1/n$ and that Ln^{3+} and Ru^{5+} ions are structurally ordered.

These compounds show complex magnetic transitions at low temperatures. These transitions are considered to be antiferromagnetic ones from large negative Weiss constants. Below the transition temperatures, there is a large difference in the temperature dependence of the magnetic susceptibility measured under the zero-field cooled condition and under the field cooled condition, which shows the existence of a weak ferromagnetic moment associated with the antiferromagnetism.

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 contain A cations at 12-coordinate sites. Double perovskite-type oxides have the formula $\text{A}_2\text{B}'\text{B}''\text{O}_6$, 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 arrangement of B' and B'' ions has been observed over the six-coordinate B sites. 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.

We have been interested in the properties of the perovskites containing pentavalent ruthenium ions. The electronic structure of Ru^{5+} is $[\text{Kr}]4d^3$ ($[\text{Kr}] = \text{krypton core}$). Such highly oxidized cations from the second transition series sometimes show quite unusual magnetic behaviour. The compounds A_2BRuO_6 (where A is an alkaline-earth metal and B is a lanthanide) contain ruthenium ions in the pentavalent state and their structural and electronic properties have been extensively investigated. If the cations A and B of the A_2BRuO_6 compounds have been selected suitably, B^{3+} and Ru^{5+} regularly order in the NaCl type, over the six-coordinate B sites. These compounds sometimes show long range magnetic ordering at low temperatures. For example, Sr_2YRuO_6 [1] and $\text{Sr}_2\text{LuRuO}_6$ [2] are antiferromagnetic below 26 and 30 K, respectively, and $\text{Sr}_2\text{ErRuO}_6$ [3] shows antiferromagnetic ordering involving both Ru^{5+} and Er^{3+} at ~ 40 K. However, previous works are limited to the compounds in which the paramagnetic ions are only Ru^{5+} ions, except for $\text{Sr}_2\text{ErRuO}_6$.

In order to investigate further the properties of ordered perovskites containing Ru^{5+} and Ln^{3+} , we have prepared $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu-Lu}$) and studied their crystal structures and magnetic properties. These compounds are expected to adopt an ordered arrangement because the difference in ionic radii between Ru^{5+} and Ln^{3+} is large (for instance, the six-coordinate ionic radii of Ru^{5+} , Eu^{3+} and Lu^{3+} are 0.565, 0.947 and 0.861 Å, respectively). In addition, they are expected to show various magnetic behaviours and magnetic transitions at low temperatures, which are thought to reflect the different electronic properties of lanthanide ions. Through study of the structurally ordered perovskites, the series of $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu-Lu}$), we can expect to obtain systematic information not only on the change of the crystal structure but also on the variation of the magnetic properties with the change of Ln^{3+} ions. In the latter case, an interesting magnetic phenomenon due to the magnetic interaction between d and f electrons will be observed.

2. Experiment

Polycrystalline samples of $\text{Sr}_2\text{LnRuO}_6$ were prepared by firing the appropriate amounts of strontium carbonate SrCO_3 , lanthanide sesquioxide Ln_2O_3 ($\text{Ln} = \text{Eu, Gd, Dy-Lu}$) or Tb_4O_7 , and ruthenium dioxide RuO_2 , first at 1173 K for 12 hours and then 1473 K for 108 hours with grinding and pelleting at regular intervals. The products were shown to be perovskite-like single phase materials by powder x-ray diffraction. Their magnetic susceptibility data were measured in a magnetic field of 0.1 T over the temperature range $6 < T < 300$ K using a SQUID magnetometer (Quantum Design, MPMSR2); magnetic susceptibility data were collected after cooling the sample from room temperature in zero applied field (ZFC) and after cooling in the measuring field (FC). The magnetization measurements were performed at 10 K over the magnetic field range $-5 < H < 5$ T.

3. Results and discussion

3.1. Crystal structure

Figure 1 shows the x-ray diffraction profiles for $\text{Sr}_2\text{LnRuO}_6$. X-ray diffraction data were analysed by the Rietveld method with the program RIETAN97 β [4]. It is found that all the compounds $\text{Sr}_2\text{LnRuO}_6$ prepared in this study have a distorted perovskite-type structure, which is monoclinic with space group $P2_1/n$. The unit cell is related to the primitive perovskite unit

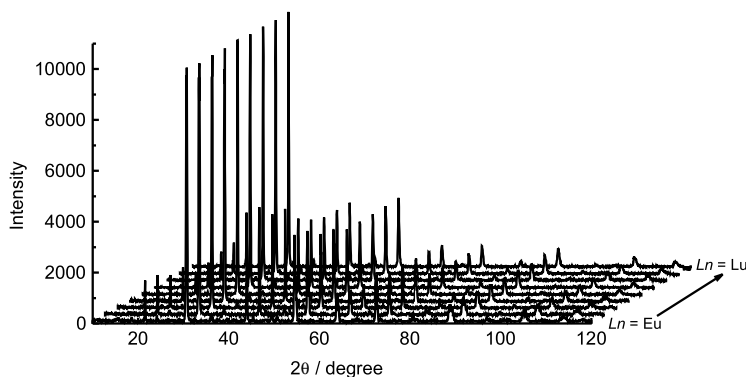


Figure 1. Powder x-ray diffraction patterns of $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu-Lu}$).

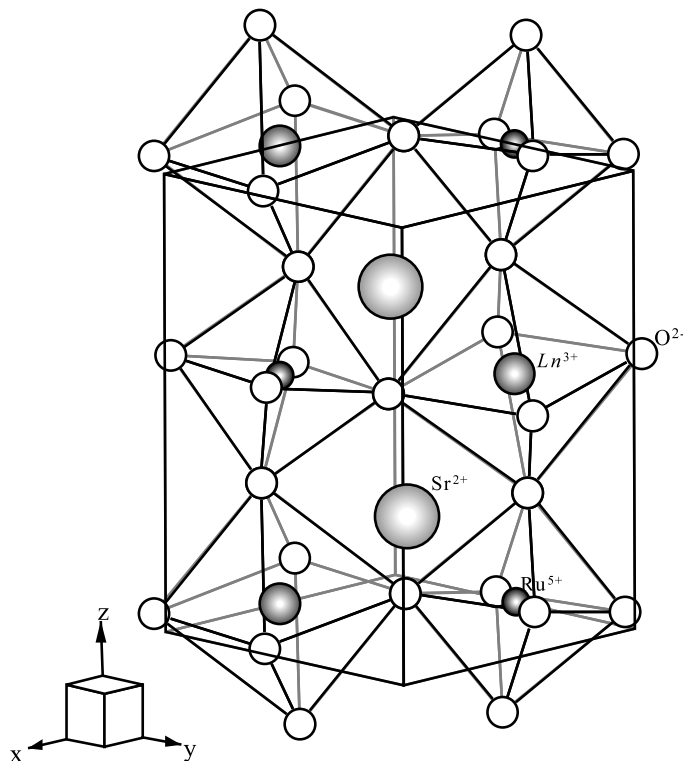


Figure 2. Crystal structure of $\text{Sr}_2\text{LnRuO}_6$ (Ln = Eu–Lu).

Table 1. Unit cell parameters and R factors for $\text{Sr}_2\text{LnRuO}_6$ (Ln = Eu–Lu).

Compound	a (Å)	b (Å)	c (Å)	β (°)	R_{wp}	R_I
$\text{Sr}_2\text{EuRuO}_6$	5.8055(2)	5.8455(2)	8.2302(2)	90.360(2)	8.53	1.58
$\text{Sr}_2\text{GdRuO}_6$	5.7978(2)	5.8317(2)	8.2165(3)	90.325(2)	9.71	2.13
$\text{Sr}_2\text{TbRuO}_6$	5.7885(6)	5.8114(4)	8.2008(8)	90.257(6)	11.61	2.90
$\text{Sr}_2\text{DyRuO}_6$	5.7777(6)	5.7974(4)	8.1821(8)	90.270(6)	12.54	2.35
$\text{Sr}_2\text{HoRuO}_6$	5.7719(6)	5.7784(5)	8.1651(9)	90.200(5)	10.89	1.77
$\text{Sr}_2\text{ErRuO}_6$	5.7611(6)	5.7644(5)	8.1449(8)	90.180(5)	11.33	1.96
$\text{Sr}_2\text{TmRuO}_6$	5.7517(6)	5.7535(6)	8.1231(6)	90.204(6)	11.79	1.96
$\text{Sr}_2\text{YbRuO}_6$	5.7430(5)	5.7431(5)	8.1046(5)	90.210(5)	12.99	2.00
$\text{Sr}_2\text{LuRuO}_6$	5.7334(5)	5.7347(5)	8.0968(5)	90.176(5)	13.18	2.46

$$R_{WP} = [\sum_k w_k |I_k(\text{obs}) - I_k(\text{calc})|^2 / \sum_k w_k I_k(\text{obs})^2]^{1/2}.$$

$$R_I = \sum_k |I_k(\text{obs}) - I_k(\text{calc})| / \sum_k I_k(\text{obs}).$$

cell (a_p) in the following way: $a \approx \sqrt{2}a_p$, $b \approx \sqrt{2}a_p$ and $c \approx 2a_p$. The Ln^{3+} and Ru^{5+} ions are arranged alternately at the B sites of the ABO_3 perovskite-type structure, i.e., they are structurally ordered over the six-coordinated sites of the $\text{Sr}_2\text{LnRuO}_6$. This crystal structure has been illustrated in figure 2.

Each lattice parameter and reliability factor R is listed in table 1. The variation of lattice parameters for $\text{Sr}_2\text{LnRuO}_6$ with the ionic radius of Ln^{3+} is displayed in figure 3. The lattice parameters a , b and c increase with the Ln^{3+} ionic radius. The lattice parameter β increases and the differences among a , b and $c/\sqrt{2}$ spread with increase of the Ln^{3+} ionic radius. This fact indicates that from Ln = Lu to Eu the crystal structures of $\text{Sr}_2\text{LnRuO}_6$ are more distorted from

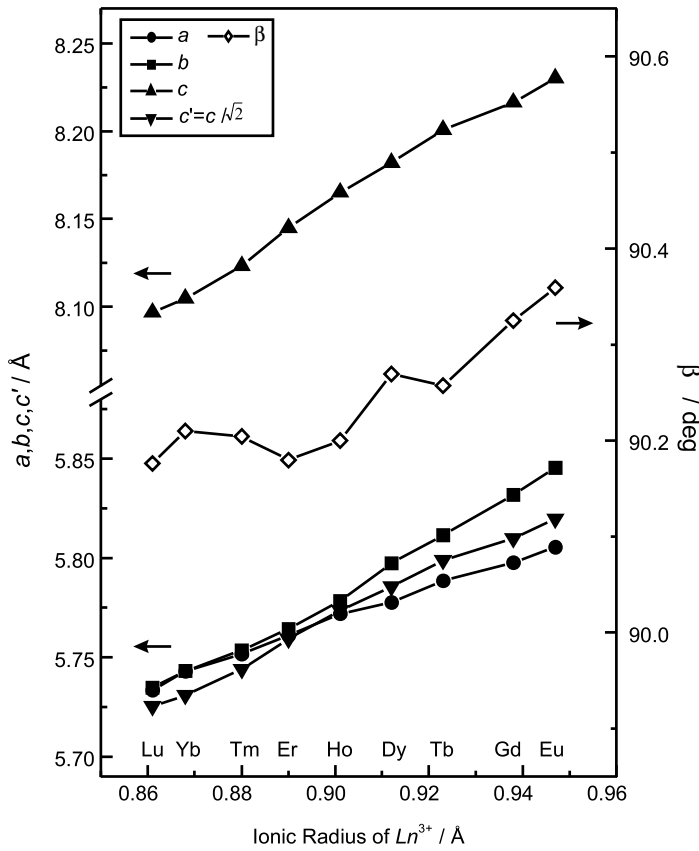


Figure 3. Variation of lattice parameters for $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu-Lu}$) with Ln^{3+} radius.

Table 2. Calculated magnetic moments for Ln^{3+} (P_{eff}), effective magnetic moments (μ_{eff}) and Weiss constants (θ) for $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Gd-Lu}$).

Ln^{3+}	P_{eff} (μ_B)	μ_{eff} (μ_B)	θ (K)
Gd^{3+} ($4f^7$)	7.94	7.1(2)	-8(1)
Tb^{3+} ($4f^8$)	9.72	9.1(1)	-15(3)
Dy^{3+} ($4f^9$)	10.63	10.4(2)	-20(3)
Ho^{3+} ($4f^{10}$)	10.58	10.6(2)	-20(3)
Er^{3+} ($4f^{11}$)	9.59	9.8(1)	-22(3)
Tm^{3+} ($4f^{12}$)	7.55	8.1(1)	-47(4)
Yb^{3+} ($4f^{13}$)	4.54	6.6(3)	-225(23)
Lu^{3+} ($4f^{14}$)	—	3.2(1)	-205(15)

the cubic symmetry. Figure 4 shows the variation of the average Ru–O bond length, the average Ln–O bond length and Ln–O–Ru angle as a function of the Ln^{3+} ionic radius. The Ru–O and Ln–O bond lengths do not change much with the ionic radius of Ln^{3+} in $\text{Sr}_2\text{LnRuO}_6$. On the other hand, the Ln–O–Ru angle decreases remarkably with the increase of Ln^{3+} ionic radius. From these results, it is found that the distortion of the double perovskite $\text{Sr}_2\text{LnRuO}_6$ from the cubic symmetry is mainly due to the tilting of the octahedra rather than to the distortion of the octahedra from the octahedral symmetry.

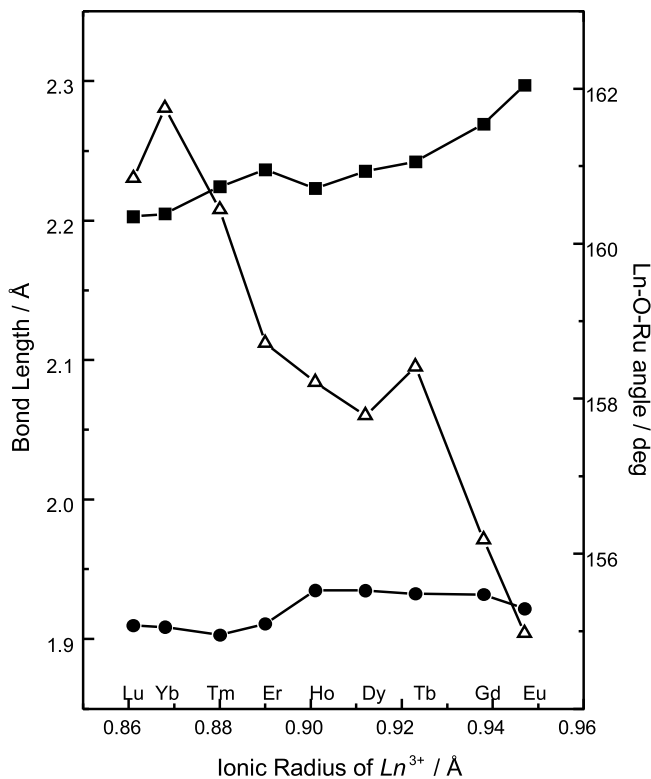


Figure 4. Average Ru–O bond length (●), Ln–O bond length (■), and Ln–O–Ru angle (△).

3.2. Magnetic properties

The molar magnetic susceptibilities of $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Eu–Lu}$) are plotted as a function of temperature in figures 5 and 6. The Curie–Weiss law is valid for the magnetic susceptibilities of $\text{Sr}_2\text{LnRuO}_6$ except for those of $\text{Sr}_2\text{EuRuO}_6$ in higher temperature range ($T > 150$ K). The effective magnetic moments (μ_{eff}) and Weiss constants (θ) of these compounds are listed in table 2. In this table, the calculated moments for the Ln^{3+} ion (free ion), P_{eff} , are also listed. It is found that the effective magnetic moments for $\text{Sr}_2\text{LnRuO}_6$ are close to the values for the Ln^{3+} ion, in spite of the fact that there exist two kinds of magnetic ion, Ln^{3+} and Ru^{5+} , in the $\text{Sr}_2\text{LnRuO}_6$ except for $\text{Ln} = \text{Lu}$. This result indicates that the contribution of the magnetic moment of the Ru^{5+} ion to the paramagnetic behaviour of $\text{Sr}_2\text{LnRuO}_6$ is negligibly small compared with that of the Ln^{3+} ion. This is in agreement with the fact that the magnetic susceptibility of $\text{Sr}_2\text{LuRuO}_6$ is considerably smaller than those of $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} \neq \text{Lu}$).

The $\text{Sr}_2\text{LnRuO}_6$ compounds show a variety of temperature dependences of magnetic susceptibilities at low temperatures as depicted in figures 5 and 6. From these measurements, we have found that the magnetic transition occurs in all of these compounds. Previous neutron diffraction experiments at 4.2 K report that $\text{Sr}_2\text{LuRuO}_6$ [2] shows an antiferromagnetic ordering of Ru^{5+} ions and that $\text{Sr}_2\text{ErRuO}_6$ [3] orders antiferromagnetically both Er^{3+} and Ru^{5+} ions. Our present magnetic susceptibility measurements on $\text{Sr}_2\text{LuRuO}_6$ and $\text{Sr}_2\text{ErRuO}_6$ show maxima in the susceptibility (ZFC)–temperature curves at 32 and 42 K, respectively. The negative Weiss constants (θ) listed in table 2 indicate that the predominant magnetic interactions in these compounds are antiferromagnetic. We consider that the magnetic interactions between Ru^{5+} ions should operate significantly because the transition temperatures do not exhibit so

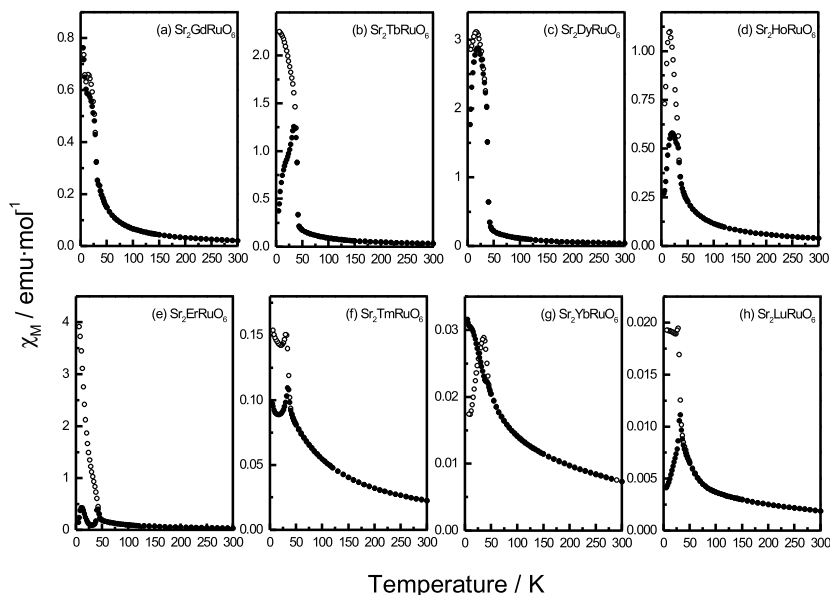


Figure 5. Temperature dependence of the ZFC (filled symbols) and FC (open symbols) molar magnetic susceptibilities for $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Gd-Lu}$).

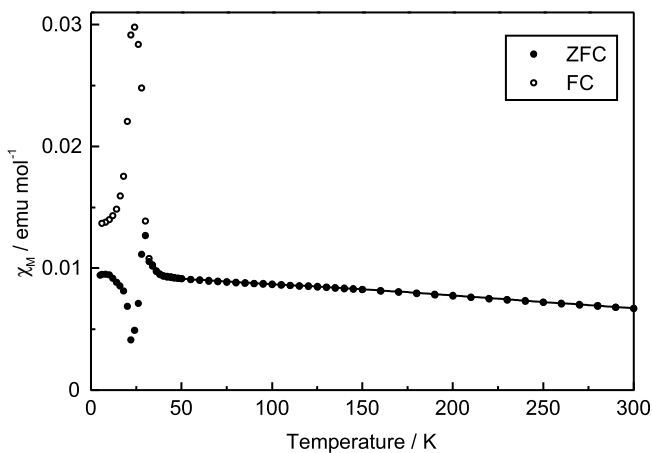


Figure 6. Temperature dependence of the ZFC (filled symbols) and FC (open symbols) molar magnetic susceptibilities for $\text{Sr}_2\text{EuRuO}_6$ and the susceptibility calculated by equation (2) (solid line).

much difference among compounds. Generally, the antiferromagnetic ordering of Ru^{5+} ions in Sr_2BRuO_6 (where B is a trivalent diamagnetic ion) is due to the superexchange interaction between nearest neighbouring Ru^{5+} ions, i.e., the pathway is Ru-O-O-Ru or Ru-O-B-O-Ru . In the present $\text{Sr}_2\text{LnRuO}_6$, two kinds of magnetic ion exist, therefore, it is thought that in addition to the magnetic interactions between Ru^{5+} ions, the interactions between Ln^{3+} and Ru^{5+} ions should also (the pathway is Ln-O-Ru) contribute to the magnetic properties of these compounds. Since the interactions between Ln^{3+} ions are generally very weak, they will not participate in the magnetic ordering. The Néel temperatures for the compounds $\text{Sr}_2\text{LnRuO}_6$ ($\text{Ln} = \text{Tb-Tm}$) are a little higher than that for $\text{Sr}_2\text{LuRuO}_6$ ($T_N = 32 \text{ K}$, Lu^{3+} is diamagnetic). This fact indicates that the magnetic interactions between Ru^{5+} and Ln^{3+} ions greatly contribute

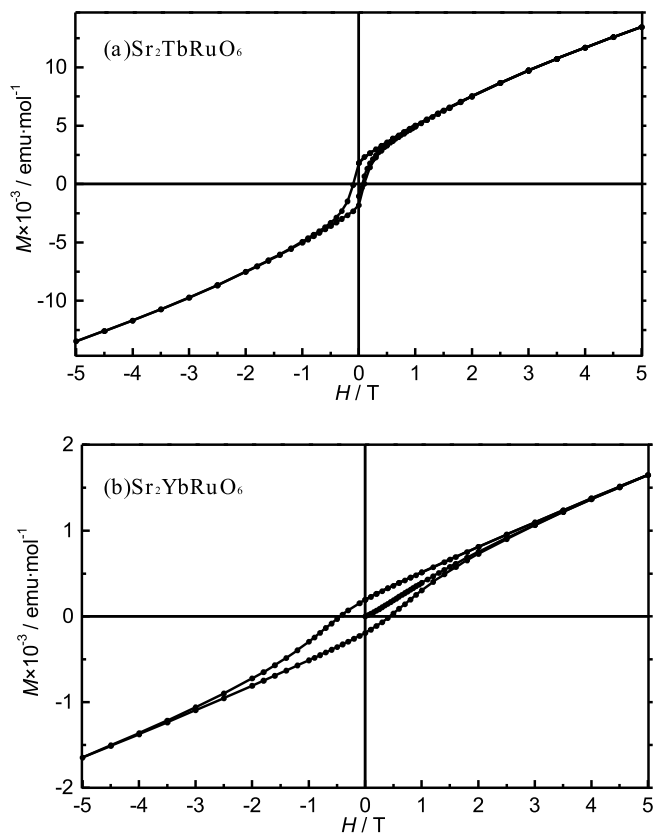


Figure 7. Variation of magnetization with the applied magnetic field at 10 K (a) for $\text{Sr}_2\text{TbRuO}_6$ and (b) for $\text{Sr}_2\text{YbRuO}_6$.

to the antiferromagnetic ordering in the $\text{Sr}_2\text{LnRuO}_6$ compounds. The Néel temperature for $\text{Sr}_2\text{SuRuO}_6$ is close to that for $\text{Sr}_2\text{LuRuO}_6$. Since the ground state of the Eu^{3+} ion is ${}^7\text{F}_0$, the magnetic interaction between Eu^{3+} and Ru^{5+} ions is negligible for this antiferromagnetic transition.

For all compounds, the field dependence of the magnetization has been measured at 10 K over the magnetic field range $-5 < H < 5$ T. Figure 7 shows the variation of magnetization as a function of magnetic field for $\text{Sr}_2\text{TbRuO}_6$ and $\text{Sr}_2\text{YbRuO}_6$. Small magnetic hysteresis has been found for all compounds. In addition to this, the large divergence between the FC and ZFC susceptibilities has been found for all compounds. These experimental results indicate that $\text{Sr}_2\text{LnRuO}_6$ are not ideal antiferromagnets. We consider that this is due to the contribution of the weak ferromagnetic component to the magnetic property. In the case of the compounds with a low crystal symmetry such as monoclinic symmetry, the Dzyaloshinsky–Moriya (D–M) interaction can exist between the ordered elements which results in the existence of a weak ferromagnetic component in their susceptibilities.

The $\text{Sr}_2\text{EuRuO}_6$ compound shows that the temperature dependence of magnetic susceptibility (figure 6) does not obey the Curie–Weiss law. The ground state ${}^7\text{F}_0$ of Eu^{3+} is nonmagnetic, and the excited states ${}^7\text{F}_J$ ($J = 1, 2, \dots, 6$) are close enough to give energy differences comparable to $k_B T$ at room temperature. The excitation to the upper states affects sufficiently the magnetic susceptibility at room temperature. Thus, the molar magnetic

susceptibility for Eu^{3+} can be expressed by the following equation [5]:

$$\chi_M(\text{Eu}^{3+}) = \frac{N_A \mu_B^2 / 3k_B}{\gamma T} \times \frac{24 + (13.5\gamma - 1.5) e^{-\gamma} + (67.5\gamma - 2.5) e^{-3\gamma} + (189\gamma - 3.5) e^{-6\gamma}}{1 + 3 e^{-\gamma} + 5 e^{-3\gamma} + 7 e^{-6\gamma}} \quad (1)$$

where the parameter $\gamma = \lambda/k_B T$ is the ratio of the multiplet width (the spin-orbit coupling constant, λ) and the thermal energy ($k_B T$), and it is 1/21 for the Eu^{3+} ion. We consider that in the paramagnetic region, the magnetic behaviour of the Eu^{3+} ion and Ru^{5+} ion are independent of each other and that the susceptibility of $\text{Sr}_2\text{EuRuO}_6$ will be given by the sum of the susceptibilities of each paramagnetic ion. If we assume that the susceptibility of Ru^{5+} follows the Curie-Weiss law, the total magnetic susceptibility of $\text{Sr}_2\text{EuRuO}_6$ will be given by

$$\chi_M = \chi_M(\text{Eu}^{3+}) + \frac{C}{T - \theta} + \chi_{TIP} \quad (2)$$

where χ_{TIP} is the temperature-independent susceptibility of $\text{Sr}_2\text{EuRuO}_6$. In order to explain the behaviour of magnetic susceptibility and to estimate the effective magnetic moment and Weiss constant of Ru^{5+} , we attempted to fit this equation (2) to experimental susceptibilities. To prevent the parameters from converging to meaningless values, we fixed the λ value on 363 cm^{-1} , which is a theoretical value (when the screening number σ is 34) and is very close to the values reported for other ordered perovskites, for example, 352 cm^{-1} ($\text{Cs}_2\text{NaEuCl}_6$) obtained from the luminescence spectra [6] and 364 cm^{-1} ($\text{Ba}_2\text{EuIrO}_6$) from the magnetic susceptibilities [7]. By this fitting, we have obtained $\mu_{eff} = 3.1(1) \mu_B$ and $\theta = -399(16) \text{ K}$. This large negative Weiss constant indicates the existence of the antiferromagnetic ordering of Ru^{5+} ions.

The magnetic susceptibility of the $\text{Sr}_2\text{YbRuO}_6$ compound shows an unusual temperature dependence, namely the ZFC magnetic susceptibility is larger than the FC magnetic susceptibility below the transition temperature and the maximum in the susceptibility-temperature curve is found only in the FC susceptibility. The large negative Weiss constant ($\theta = -225(23) \text{ K}$) indicates the existence of the antiferromagnetic interaction. Since the effective magnetic moment of Yb^{3+} is not so large compared with that of Ru^{5+} ion, the magnetic behaviour of $\text{Sr}_2\text{YbRuO}_6$ should be similar to that of $\text{Sr}_2\text{LuRuO}_6$. However, experimental results are quite different between them, i.e., abnormal temperature dependence of the susceptibility has been found for $\text{Sr}_2\text{YbRuO}_6$.

In conclusion, we have found complex magnetic behaviour of $\text{Sr}_2\text{LnRuO}_6$ which is ascribable to the magnetic coupling between 4d electrons and 4f electrons. These materials need to be investigated further using methods such as specific heat and neutron diffraction measurements, the latter to interpret the actual magnetic ordering.

Acknowledgment

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References

- [1] Battle P D and Macklin W J 1984 *J. Solid State Chem.* **52** 138
- [2] Battle P D and Jones C W 1989 *J. Solid State Chem.* **78** 108
- [3] Battle P D, Jones C W and Studer R 1991 *J. Solid State Chem.* **90** 302
- [4] Izumi F 1993 *The Rietveld Method* ed R A Young (Oxford: Oxford University Press) ch 13
- [5] Van Vleck J H 1931 *The Theory of Electric and Magnetic Susceptibilities* (Oxford: Oxford University Press)
- [6] Flint C D and Stewart-Darling F L 1981 *Mol. Phys.* **44** 61
- [7] Wakeshima M, Harada D, Hinatsu Y and Masaki N 1999 *J. Solid State Chem.* at press