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Magnetic properties of ruthenium pyrochlores $R_2Ru_2O_7$ (R = rare earth)

Nobuyuki Taira, Makoto Wakeshima and Yukio Hinatsu

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

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Abstract. Magnetic susceptibility and magnetic hysteresis measurements were performed for rare earth pyrochlores $R_2Ru_2O_7$ (R = Pr, Nd and Sm–Yb). The compounds of R = Pr, Nd, Sm and Eu show magnetic transitions at 165, 150, 135 and 120 K, respectively. Below the transition temperatures, there is a large difference in the temperature dependence of the magnetization measured under zero-field-cooled conditions (ZFC) and under field-cooled conditions (FC), but no magnetic hysteresis has been observed. These results show that below the transition temperatures, the magnetic state of these pyrochlores transforms to a spin-glass state. When the temperature is further decreased through ~ 20 K, apparent cusps have been observed for R = Nd, Sm and Eu in the susceptibility–temperature curves. Magnetic hysteresis measurements at 5.0 K indicate that there is a possibility of a contribution of weak ferromagnetism to the magnetic behaviour of $Sm_2Ru_2O_7$ at very low temperatures. That is, at these very low temperatures, both the spin-glass state and a weak ferromagnetic state may coexist for $Sm_2Ru_2O_7$.

1. Introduction

Ruthenium has many oxidation states, ranging from +2 to +8. Many complex oxides contain ruthenium ions in these various oxidation states. We have been interested in oxides containing Ru^{4+} with an electronic configuration $[Kr] 4d^4$, where $[Kr]$ is the krypton core. The aim of this study is to characterize the electronic properties of the Ru^{4+} cation in pyrochlores, and to determine the extent to which the outer $4d^4$ electrons are delocalized. The magnetic behaviour is a useful indicator of the degree of localization/delocalization in that a localized electron system is expected to show long-range magnetic order at low temperatures.

The oxidation states for the $A_2M_2O_7$ configuration are generally $A_2^{2+}M_2^{5+}O_7^{2-}$ or $A_2^{3+}M_2^{4+}O_7^{2-}$ [1]. We are interested in the latter formulation, i.e. in those pyrochlores for which the A cation is a trivalent rare earth: $R_2^{3+}M_2^{4+}O_7^{2-}$.

Rare earth pyrochlores show a wide diversity of properties. Some are electrical insulators, and others are low-activation-energy semiconductors [2–4]. In addition to diamagnetism and paramagnetism, ferromagnetism is also encountered in some rare earth pyrochlores [5–8].

The ruthenium pyrochlore oxides $R_2Ru_2O_7$ have been extensively studied for their novel conductivity [9, 10] and catalytic activity [11, 12]. Previously, we reported the results of magnetic susceptibility and magnetic hysteresis measurements on $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ [13]. Both compounds show magnetic transitions at 80 and 85 K, respectively. Below these temperatures, they transform to a spin-glass state. In these compounds, the magnetic properties should be attributable to the properties of the Ru^{4+} ions in the pyrochlore structure, because both the Y^{3+} ion and the Lu^{3+} ion are diamagnetic.

In this study, we have paid attention to the ruthenium pyrochlores $R_2Ru_2O_7$ in which rare earth ions (R^{3+} ions) are also paramagnetic. The synthesis, the crystal structure determination and magnetic properties of $R_2Ru_2O_7$ where $R = Pr, Nd,$ and $Sm\text{--}Yb$ will be reported.

2. Experiment

2.1. Sample preparation

The samples were prepared by decomposing well mixed solid nitrates, because they are difficult to prepare by the direct reaction of oxides. The rare earth oxides R_2O_3 ($R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm$ and Yb), Pr_6O_{11} , Tb_4O_7 and ruthenium dioxide RuO_2 were weighed in the correct ratios and dissolved in concentrated nitric acid. The excess nitric acid was removed by gentle heating. The remaining powders were slowly heated to $400\text{ }^\circ\text{C}$ for 1 h and heated at $850\text{ }^\circ\text{C}$ for 12 h. After cooling to room temperature, the samples were crushed into powder, reground, pressed into pellets and then reheated at $900\text{--}1200\text{ }^\circ\text{C}$, with several intermediate regrindings.

2.2. Analysis

X-ray powder diffraction measurements were performed with $Cu\ K\alpha$ radiation on a Rigaku Rint 2000 diffractometer equipped with a curved graphite monochromator. Intensity data were collected by step scanning in the range between 10 and 120° at intervals of 0.04° . The structure and lattice parameters were refined with a Rietveld program RIETAN [14].

2.3. Magnetic measurements

Magnetic susceptibility, magnetic hysteresis and residual magnetization measurements were performed with a SQUID magnetometer (Quantum Design model MPMS). The temperature dependence of the magnetic susceptibilities was investigated under zero-field-cooled conditions (ZFC) and field-cooled conditions (FC). The former was measured in a residual magnetization mode on heating the sample to 300 K at 0.1 T after zero-field cooling to 2.0 K. The latter was measured on cooling the sample from 300 to 2.0 K at 0.1 T. Magnetic hysteresis (the field dependence of the magnetization) was measured at 5.0 K and 40 K by changing the applied magnetic field between -5.0 T and 5.0 T. Residual magnetization measurement was performed by two kinds of conditions; the ZFC residual magnetization was measured on heating the sample to 150 K after zero-field cooling to 2.0 K, applying a magnetic field of 5.0 T, and then reducing it to zero. The FC residual magnetization was measured on heating the sample to 150 K after cooling in a magnetic field of 5.0T, and then reducing the magnetic field to zero.

3. Results and discussion

X-ray diffraction measurements show that the desired pyrochlore-type compounds $R_2Ru_2O_7$ ($R = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm$ and Yb) could be prepared as single-phase materials. Their lattice parameters are shown in table 1, and are in excellent agreement with those reported by other workers [15, 16].

Table 1. Lattice parameters for $R_2Ru_2O_7$.

	Lattice parameter (\AA)
$Pr_2Ru_2O_7$	10.3733(1)
$Nd_2Ru_2O_7$	10.3450(2)
$Sm_2Ru_2O_7$	10.2813(3)
$Eu_2Ru_2O_7$	10.2566(2)
$Gd_2Ru_2O_7$	10.2357(1)
$Tb_2Ru_2O_7$	10.1961(8)
$Dy_2Ru_2O_7$	10.1714(1)
$Ho_2Ru_2O_7$	10.1468(2)
$Er_2Ru_2O_7$	10.1213(1)
$Tm_2Ru_2O_7$	10.0985(2)
$Yb_2Ru_2O_7$	10.0751(3)

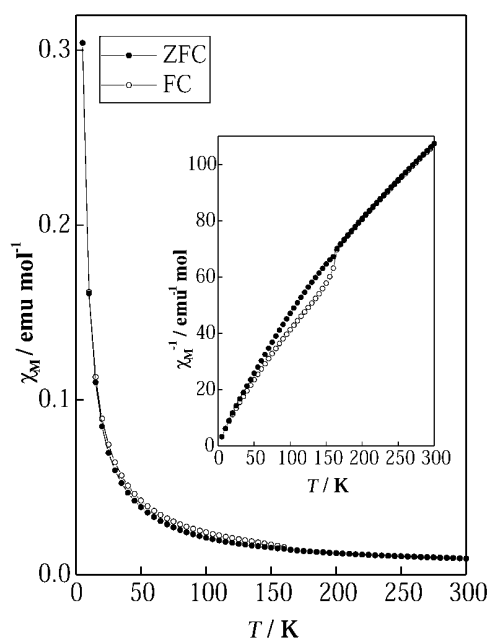


Figure 1. Temperature dependence of the susceptibilities for $Pr_2Ru_2O_7$. The applied magnetic field is 0.1 T. Filled symbols (\bullet) correspond to ZFC susceptibilities and open symbols (\circ) correspond to FC susceptibilities. The inset shows the temperature dependence of the inverse susceptibilities.

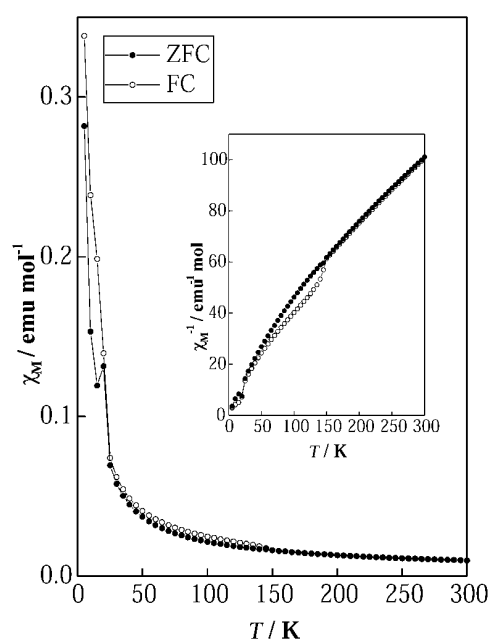


Figure 2. Temperature dependence of the susceptibilities for $Nd_2Ru_2O_7$. The applied magnetic field is 0.1 T. The inset shows the temperature dependence of the inverse susceptibilities.

3.1. $Pr_2Ru_2O_7$

Figure 1 shows the temperature dependence of the susceptibility for $Pr_2Ru_2O_7$. It shows a magnetic transition at 165 K. Our experimental results are quite different from those of previous workers [17], who reported that $Pr_2Ru_2O_7$ remains paramagnetic down to 2.0 K. The magnetic susceptibilities measured under zero-field-cooled conditions (ZFC) and under the field-cooled conditions (FC) show a slightly different temperature dependence below the transition temperature.

3.2. $\text{Nd}_2\text{Ru}_2\text{O}_7$

Figure 2 shows the temperature dependence of the susceptibility for $\text{Nd}_2\text{Ru}_2\text{O}_7$. It is found that the ZFC and FC magnetic susceptibilities diverge below 150 K, and that the ZFC magnetic susceptibility shows the existence of a magnetic transition at 20 K. Continuous change in both the transition temperature and the magnetic susceptibility–temperature behaviour with the applied magnetic field has been found for $\text{Nd}_2\text{Ru}_2\text{O}_7$, while such a significant change was not observed for $\text{Y}_2\text{Ru}_2\text{O}_7$ and $\text{Lu}_2\text{Ru}_2\text{O}_7$ [13]. With increasing applied magnetic field, the divergence of the ZFC and FC magnetic susceptibilities becomes less prominent, and no divergence is observed at an applied field of 1.0 T (see figure 3). The field dependence of the magnetization for $\text{Nd}_2\text{Ru}_2\text{O}_7$ is shown in figure 4. A magnetic hysteresis loop is observed, although its magnitude is very small. The results of the FC magnetization measurements are similar to those for the ZFC magnetization, which is quite different from the $\text{Y}_2\text{Ru}_2\text{O}_7$ case. In the $\text{Y}_2\text{Ru}_2\text{O}_7$, no magnetic hysteresis was observed, but the measurement of the FC magnetization differ from those of the ZFC magnetization [13].

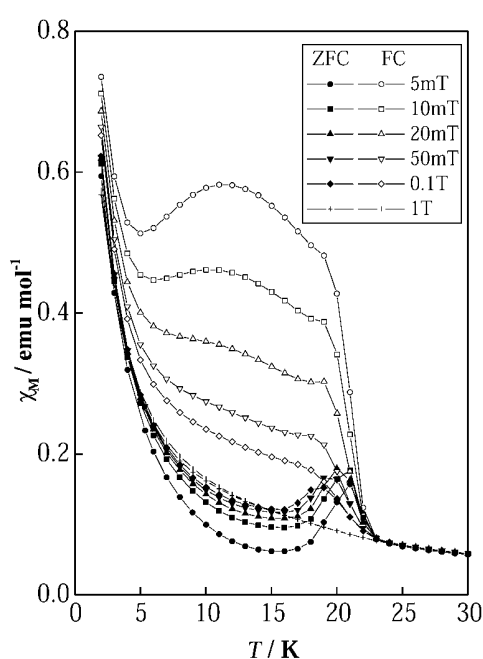


Figure 3. Susceptibility–temperature curves at various applied magnetic fields in the low temperature region for $\text{Nd}_2\text{Ru}_2\text{O}_7$.

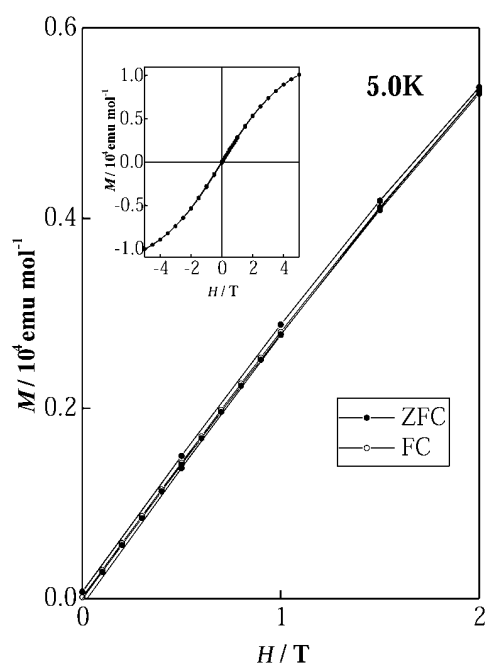


Figure 4. Magnetic hysteresis curves (field dependence of the magnetization) for $\text{Nd}_2\text{Ru}_2\text{O}_7$ at 5.0 K.

3.3. $\text{Sm}_2\text{Ru}_2\text{O}_7$

The temperature dependence of the susceptibility for $\text{Sm}_2\text{Ru}_2\text{O}_7$ is shown in figure 5. The magnetic transition is observed at 135 K, and remarkable divergence between the ZFC and the FC susceptibilities is found below the transition temperature. This magnetic divergence is much more pronounced than those for $\text{Pr}_2\text{Ru}_2\text{O}_7$ and $\text{Nd}_2\text{Ru}_2\text{O}_7$. In addition, another magnetic transition is observed at ~ 20 K. Magnetic hysteresis measurements for $\text{Sm}_2\text{Ru}_2\text{O}_7$ have been performed both at 40 K (a temperature between the two transition temperatures) and at 5.0 K

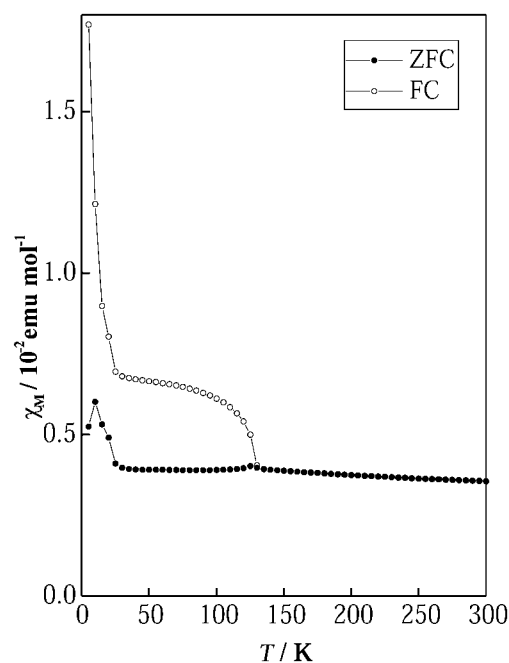


Figure 5. Temperature dependence of the susceptibilities for $\text{Sm}_2\text{Ru}_2\text{O}_7$. The applied magnetic field is 0.1 T.

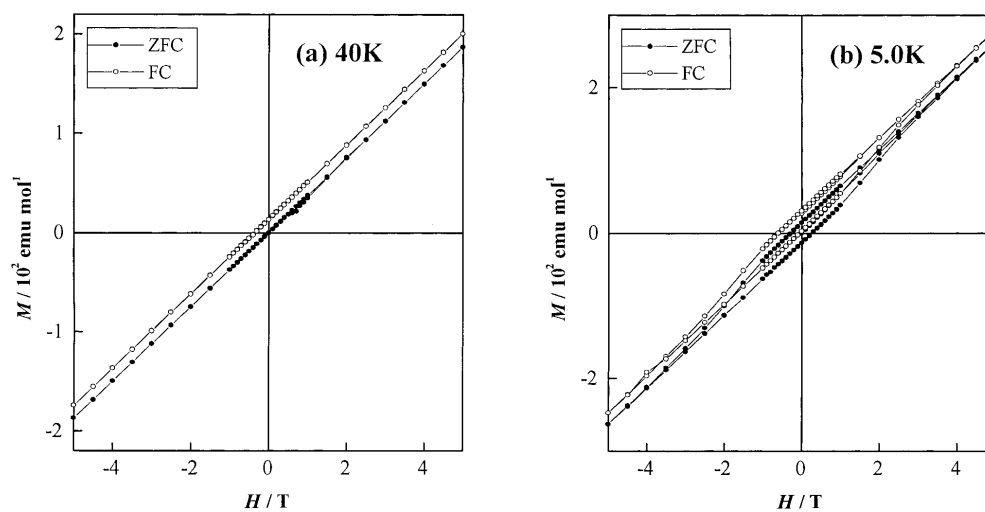


Figure 6. Magnetic hysteresis curves for $\text{Sm}_2\text{Ru}_2\text{O}_7$ at (a) 40 K and (b) 5.0 K.

(below the lower transition temperature), and the results are shown in figure 6. At 40 K, no magnetic hysteresis is observed, but the measurements of FC magnetization differ from those of the ZFC magnetization. When the temperature is decreased to 5.0 K, the magnetic hysteresis is observed in addition to the difference in the ZFC magnetization and FC magnetization. Figure 7 shows the results of residual magnetization measurements for $\text{Sm}_2\text{Ru}_2\text{O}_7$. We have performed two kinds of measurement; the first (ZFC) was measured on heating the sample to

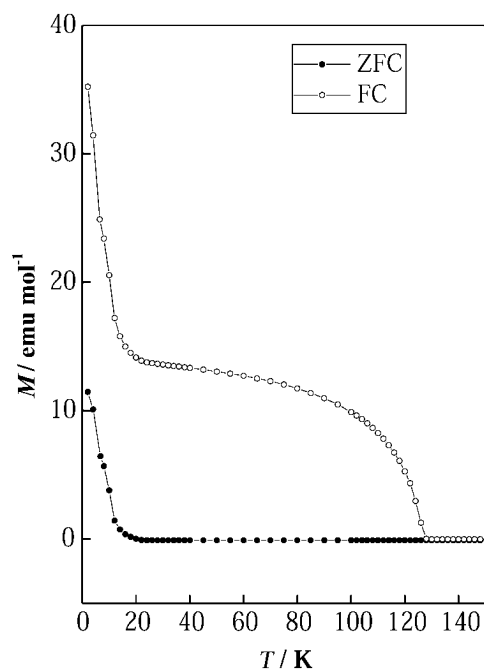


Figure 7. Temperature dependence of the residual magnetization for $\text{Sm}_2\text{Ru}_2\text{O}_7$.

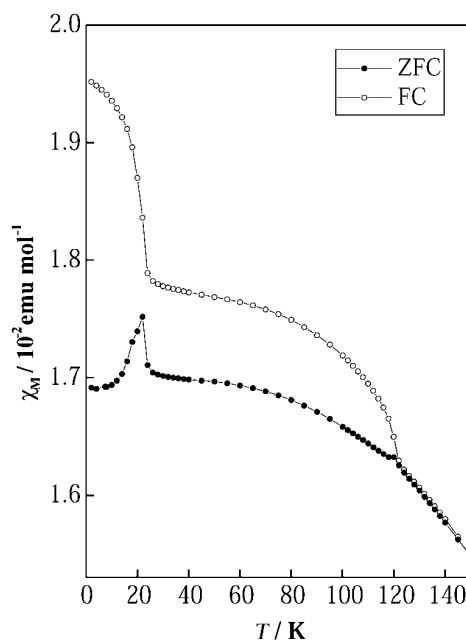


Figure 8. Temperature dependence of the susceptibilities for $\text{Eu}_2\text{Ru}_2\text{O}_7$ at 2–150 K. The applied magnetic field is 0.1 T.

150 K after zero-field cooling to 2.0 K, applying a magnetic field of 5.0 T, and then reducing it to zero. The second measurement (FC) was measured on heating the sample to 150 K after cooling in a 5.0 T, and then reducing the magnetic field to zero. The residual magnetization measured under ZFC differs greatly from that measured under FC (see figure 7). The residual magnetization decreases with increasing temperature, and the ZFC residual magnetization disappears at 20 K and the FC residual magnetization disappears at 135 K. These temperatures are in accord with the magnetic transition temperatures.

3.4. $\text{Eu}_2\text{Ru}_2\text{O}_7$

Figure 8 shows the temperature dependence of the susceptibility for $\text{Eu}_2\text{Ru}_2\text{O}_7$. The divergence of the ZFC and the FC susceptibilities is found below 120 K, with a small cusp at 120 K in the ZFC susceptibility. The divergence and the small cusp probably indicate the existence of a strong magnetic interaction between ruthenium ions. With further decreasing temperature, a sharp cusp is observed in the ZFC susceptibility at 22 K and the FC susceptibility suddenly increases through this temperature. No magnetic hysteresis is observed and the measurements of FC magnetization differ from those of the ZFC magnetization, which is similar to the results for $\text{Y}_2\text{Ru}_2\text{O}_7$. Figure 9 shows the results of residual magnetization measurements for $\text{Eu}_2\text{Ru}_2\text{O}_7$. The residual magnetization decreases with increasing temperature; the ZFC residual magnetization disappears at ~ 20 K and the FC residual magnetization disappears at 120 K. These temperatures accord with the magnetic transition temperatures of $\text{Eu}_2\text{Ru}_2\text{O}_7$.

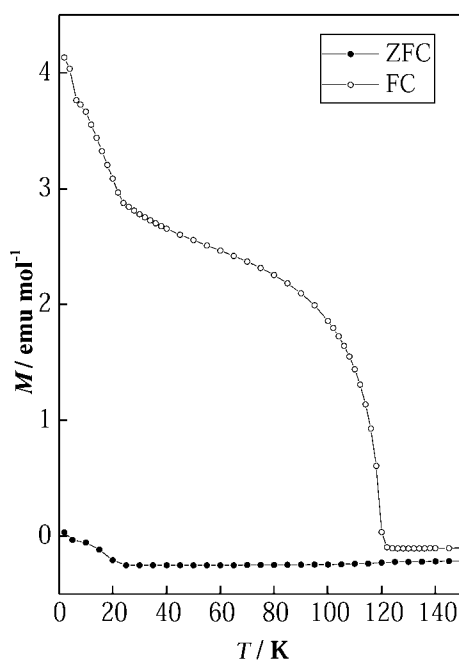


Figure 9. Temperature dependence of the residual magnetization for $\text{Eu}_2\text{Ru}_2\text{O}_7$.

3.5. Other pyrochlores $R_2\text{Ru}_2\text{O}_7$ ($R = \text{Gd}-\text{Yb}$)

No magnetic transition is observed for any of the other ruthenium pyrochlores $R_2\text{Ru}_2\text{O}_7$ ($R = \text{Gd}-\text{Yb}$) in the temperature range 5–300 K.

3.6. Trends in the magnetic properties of rare earth pyrochlores

In this study, we focus our attention on the magnetic properties of ruthenium pyrochlores $R_2\text{Ru}_2\text{O}_7$, where $R = \text{Pr}$, Nd and $\text{Sm}-\text{Yb}$. The divergence of ZFC and FC susceptibilities is observed below the magnetic transition temperatures for $\text{Pr}_2\text{Ru}_2\text{O}_7$ (165 K), $\text{Nd}_2\text{Ru}_2\text{O}_7$ (150 K), $\text{Sm}_2\text{Ru}_2\text{O}_7$ (135 K) and $\text{Eu}_2\text{Ru}_2\text{O}_7$ (120 K). The smaller the ionic radius of the rare earth is, the lower the transition temperature is. In the lower temperature region, the ZFC susceptibility shows a sharp cusp at ~ 20 K for $\text{Nd}_2\text{Ru}_2\text{O}_7$, $\text{Sm}_2\text{Ru}_2\text{O}_7$ and $\text{Eu}_2\text{Ru}_2\text{O}_7$. These results are in contrast to those of $\text{Y}_2\text{Ru}_2\text{O}_7$ and $\text{Lu}_2\text{Ru}_2\text{O}_7$ which have no cusp in the magnetic susceptibility–temperature curve below 20 K.

Below the magnetic transition temperatures, no magnetic hysteresis loop is observed, but the FC magnetization differs from the ZFC magnetization. This behaviour is a spin-glass one. When the temperature is further decreased below 20 K, a magnetic hysteresis loop is observed, indicating that a weak ferromagnetic component also contributes to the magnetic behaviour of $R_2\text{Ru}_2\text{O}_7$.

The results of the residual magnetization measurements are also important. Although the ZFC residual magnetization becomes zero at 20 K, the FC residual magnetization still exists above this temperature and finally disappears at the magnetic transition temperature.

The present experimental results indicate that below the transition temperature (the temperature at which the ZFC and FC magnetic susceptibilities diverge), the magnetic state for $\text{Nd}_2\text{Ru}_2\text{O}_7$, $\text{Sm}_2\text{Ru}_2\text{O}_7$ and $\text{Eu}_2\text{Ru}_2\text{O}_7$ transforms to a spin-glass state, and when the

temperature is further decreased through ~ 20 K, a weak ferromagnetic state coexists with the spin-glass state.

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