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Specific Heat and ac Susceptibility Studies on Ruthenium Pyrochlores $R_2Ru_2O_7$ (R = Rare Earths)

Nobuyuki Taira, Makoto Wakeshima, and Yukio Hinatsu

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

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Specific heat and ac susceptibility measurements were performed for $R_2Ru_2O_7$ (R = Y, Pr, Nd, Sm, Eu, and Lu). For $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$, a λ-type specific heat anomaly has been observed at 77 and 78 K, respectively, which is consistent with the magnetic transition found in their magnetic susceptibility vs temperature curves. In the real part of the ac susceptibilities, small cusps are observed at 78 K for $Y_2Ru_2O_7$ and at 80 K for $Lu_2Ru_2O_7$. Both the real part and the imaginary part of the ac susceptibilities are independent of frequency, indicating that these compounds are not in the ordinary spin-glass. Similar large jumps of specific heat are observed at 162, 143, 124, and 118 K for $R_2Ru_2O_7$ (R = Pr, Nd, Sm, and Eu). For $Sm_2Ru_2O_7$ and $Eu_2Ru_2O_7$, no specific heat anomaly has been found at lower temperatures, although magnetic anomaly was observed at ca. 20 K in their dc susceptibility vs temperature curves. ac susceptibility measurements show that both the real and the imaginary susceptibilities show anomaly at ca. 20 K and this temperature decreases with decreasing frequency. These results strongly indicate that the transition observed at ca. 20 K is the spin-glass one. The experimental results on $Nd_2Ru_2O_7$ show that magnetic properties of this compound are complicated. © 2000 Academic Press

INTRODUCTION

In an early work, we reported the results of magnetic susceptibility and magnetic hysteresis measurements on $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ (1). Both compounds show magnetic transitions at 80 and 85 K, respectively. Below these temperatures, they transform to a spin-glass state. Their magnetic properties should be attributable to the behavior of the Ru^{4+} ions in the pyrochlore structure, because both the Y^{3+} ion and the Lu^{3+} ion are diamagnetic.

In the following, we paid attention to the ruthenium pyrochlores $R_2Ru_2O_7$ in which not only the ruthenium ion but also rare earth ions (R^{3+} ions) are paramagnetic, and measured magnetic properties for $R_2Ru_2O_7$ where R = Pr, Nd, and Sm–Yb (2). Among them, $Pr_2Ru_2O_7$, $Nd_2Ru_2O_7$, $Sm_2Ru_2O_7$, and $Eu_2Ru_2O_7$ show magnetic transitions at 165, 150, 135, and 120 K, respectively, and the divergence of ZFC (zero-field-cooled condition) and FC (field-cooled condition) susceptibilities is observed below the magnetic transition temperatures. The transition temperature has been found to become lower with decreasing the ionic radius of rare earth in these ruthenium pyrochlores. In the lower temperature region, the ZFC susceptibility shows a sharp cusp at ca. 20 K for $Nd_2Ru_2O_7$, $Sm_2Ru_2O_7$, and $Eu_2Ru_2O_7$. Below the magnetic transition temperatures, no magnetic hysteresis loop is observed, but the FC magnetization differs from the ZFC magnetization, which shows that this behavior is a spin-glass one. When the temperature is furthermore decreased below 20 K, magnetic hysteresis loop is observed, indicating that a weak ferromagnetic component also contributes to the magnetic behavior of $R_2Ru_2O_7$. Our previous experimental results indicate that below the transition temperature (120–150 K), the magnetic state for $Nd_2Ru_2O_7$, $Sm_2Ru_2O_7$, and $Eu_2Ru_2O_7$ transforms to a spin-glass state, and when the temperature is still decreased through ca. 20 K, a weak ferromagnetic state coexists with the spin-glass state.

In this study, we have performed the ac susceptibility and specific heat measurements for the $R_2Ru_2O_7$ (R = Y, Pr, Nd, Sm, Eu, and Lu) in order to investigate the nature of magnetic ordering found in these ruthenium pyrochlores.

EXPERIMENTAL

Preparation of Samples

The sample preparation and analysis have been described previously (1, 2). The starting materials, R_2O_3 powder (the purity is more than 99.9%), Pr_6O_{11} powder (99.9%), and RuO_2 powder (99.9%), were dissolved in a concentrated nitric acid. The excess nitric acid was removed, and the remaining powders were slowly heated to 400°C and then heated at 850°C and finally heated at 1100–1200°C for 72–96 h.

Specific Heat Measurements

The specific heat of the samples was measured in the temperature range 1.8–200 K using a relaxation technique

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supplied by the commercial heat capacity measurement system (Quantum Design, PPMS model). The sample in the form of pellet ($\sim$10 mg) was mounted on an alumina plate with apiezon for better thermal contact.

ac Susceptibility Measurements

The ac magnetic susceptibility measurement was performed with the same measurement system (Quantum Design, PPMS model). The temperature dependence of the ac magnetic susceptibilities was investigated at various frequencies. The samples were first cooled in a zero magnetic field and then an ac field was applied up to 15Oe. For each temperature, ac frequency was changed from 80 to 8888 Hz.

RESULTS AND DISCUSSION

A. Specific Heat

Figure 1 shows the temperature dependence of the specific heat for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$. It shows a large jump of the specific heat at 77 K for $R = Y$, in agreement with the another worker's report (3). For $R = Lu$, similar large jump can be observed at 78 K. The temperatures for these λ-type anomalies found in the specific heat vs temperature curves correspond to the temperatures for small cusps in the ZFC susceptibility vs temperature curves (1). At low temperatures, the specific heat C can be well described by the relation $C = \gamma T + \beta T^3$. The values of γ for these two compounds are determined by the least squares fitting in the temperature range below 7 K. They are 5 (for $Y_2Ru_2O_7$)

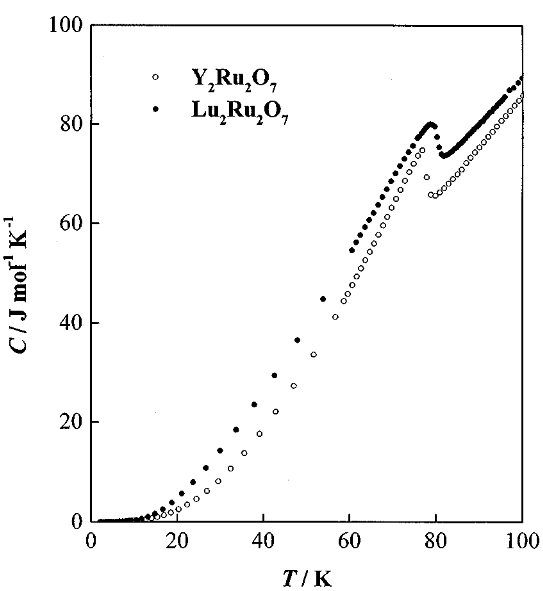

FIG. 1. Temperature dependence of the specific heat for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$. Open symbols (○) correspond to $Y_2Ru_2O_7$ and filled symbols (●) correspond to $Lu_2Ru_2O_7$.

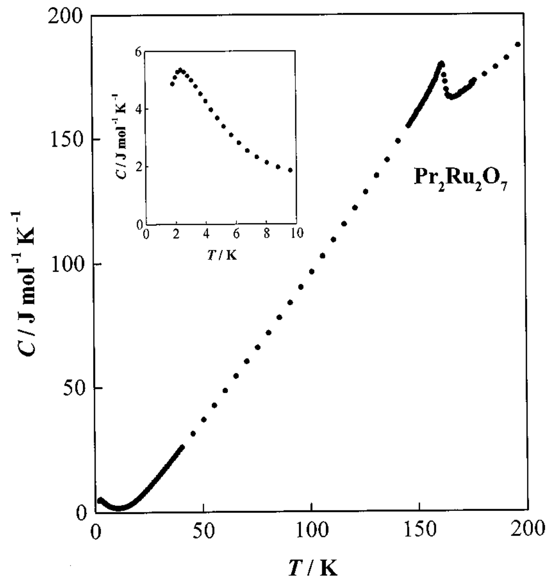

FIG. 2. Temperature dependence of the specific heat for $Pr_2Ru_2O_7$. The inset shows the lower temperature data.

and 3 (for $Lu_2Ru_2O_7$) mJ/K^2 mol, which are good in agreement with the results reported previously (3, 4). These experimental results are contrastive to the case for the spin-glass molybdenum pyrochlore (5), where a broad peak is seen at its spin-glass transition temperature in the specific heat vs temperature curve. The present result indicates the existence of the long-range magnetic order for both $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$.

The results on the specific heat measurements for $R_2Ru_2O_7$ (R = Pr, Nd, Sm, and Eu) are shown in Figs. 2–4. Sharp λ-type peaks are observed for any of these compounds. Their temperatures are 162, 143, 124, and 118 K for R = Pr, Nd, Sm, and Eu, respectively. These temperatures correspond to the temperatures for the cusps found in the ZFC susceptibility vs temperature curves (2). In the susceptibility vs temperature curves for $Sm_2Ru_2O_7$ and $Eu_2Ru_2O_7$, another magnetic anomaly has been observed at lower temperatures (ca. 20 K). However, no anomaly has been found in their specific heat vs temperature curves, and the temperature dependence of specific heat for these compounds (Fig. 4) is similar to that for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ (Fig. 1). Since the specific heat data for $Sm_2Ru_2O_7$ were not well described by the expression $C = \gamma T + \beta T^3$, the value of γ was not determined. For $Eu_2Ru_2O_7$, the value of γ is obtained to be 3 mJ/K^{2}mol.

The temperature dependence of specific heat for $Nd_2Ru_2O_7$ is peculiar (see Fig. 3). In addition to the λ-type specific heat anomaly at 143 K, another jump of specific heat is found at ca. 20 K. This anomaly corresponds to the magnetic transition found in its magnetic susceptibility vs temperature curve. With decreasing temperature, the speci-

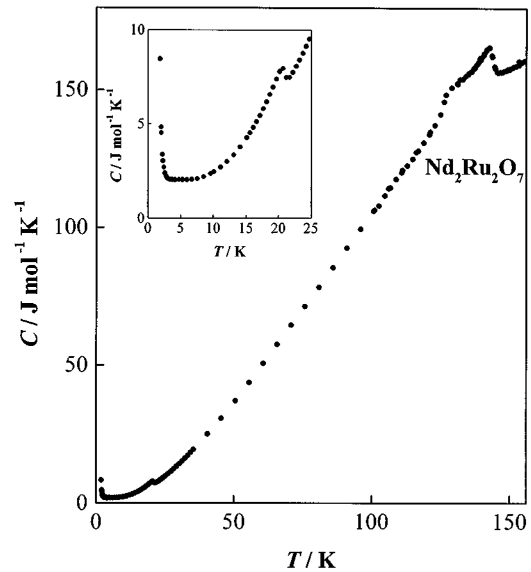

FIG. 3. Temperature dependence of the specific heat for $Nd_2Ru_2O_7$. The inset shows the lower temperature data.

fic heat decreases down to 3 K, and it suddenly increases through this temperature. $Pr_2Ru_2O_7$ shows the Schottky-like specific heat anomaly at ca. 2 K in addition to the λ-type anomaly at 162 K (Fig. 2).

B. ac Susceptibility

Figures 5a and 5b show the temperature dependence of the ac susceptibilities for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ in the

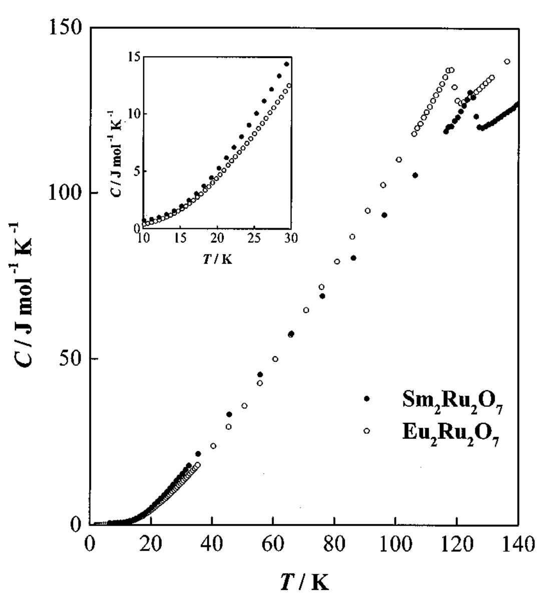

FIG. 4. Temperature dependence of the specific heat for $Sm_2Ru_2O_7$ and $Eu_2Ru_2O_7$. Filled symbols (●) correspond to $Sm_2Ru_2O_7$ and open symbols (○) correspond to $Eu_2Ru_2O_7$. The inset shows the lower temperature data.

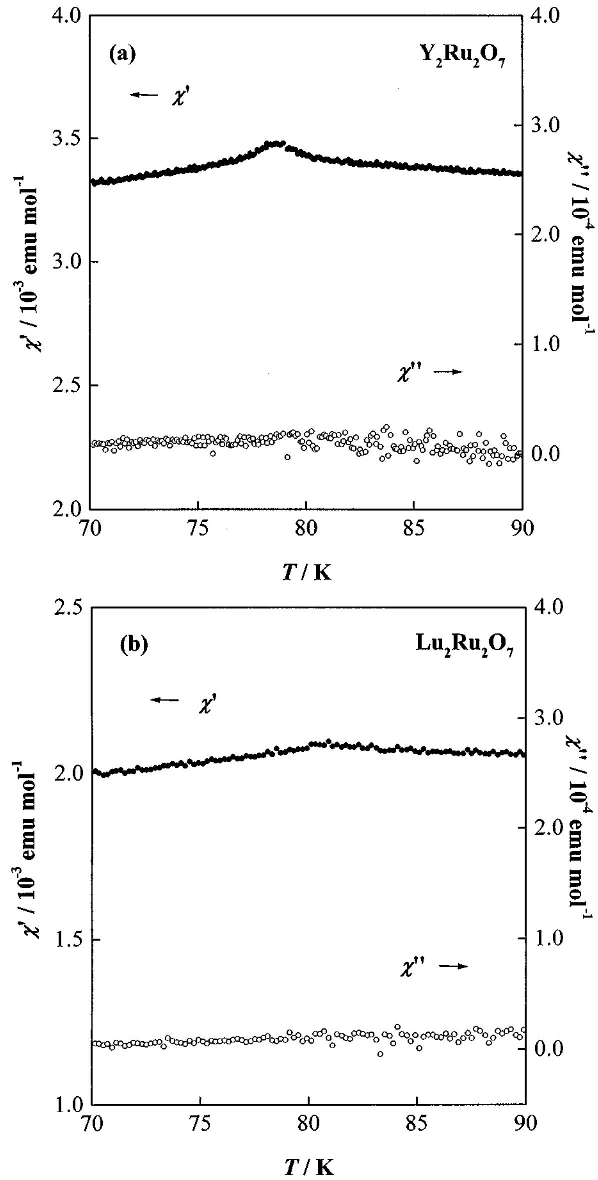

FIG. 5. Temperature dependence of ac susceptibilities for (a) $Y_2Ru_2O_7$ and (b) $Lu_2Ru_2O_7$.

temperature range between 70 and 90 K. In the real part χ' of the susceptibilities, small cusps are observed at 78 K for $R = Y$ and at 80 K for $R = Lu$, which is similar to the dc ZFC susceptibilities (1). On the other hand, the imaginary part χ'' of the susceptibilities for both the compounds show no anomaly in the whole temperature range studied. Both the real χ' and the imaginary χ'' susceptibilities are independent of frequency. The experimental results that the large jump of the specific heat is observed at ca. 80 K and that the ac susceptibilities are independent of frequency show that $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ are not ordinary spin-glass compounds.

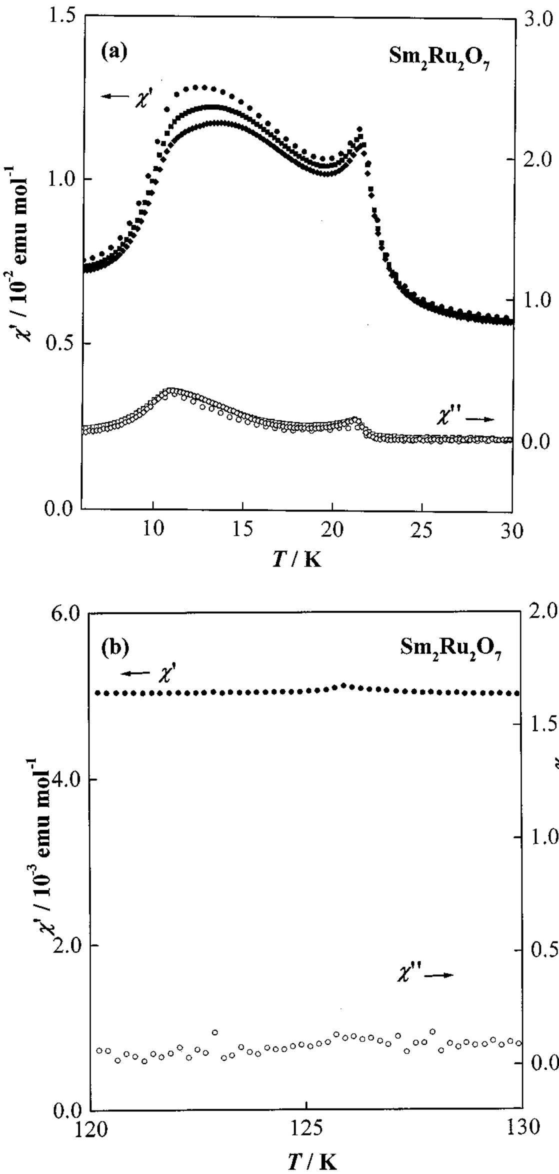

FIG. 6. Temperature dependence of ac susceptibilities for $Sm_2Ru_2O_7$ in the temperature range between (a) 6 and 30 K and (b) 120 and 130 K. (●, ○) 80 Hz, (■, □) 888 Hz, (◆, ◇) 8888 Hz.

The temperature dependence of the ac susceptibilities for $R_2Ru_2O_7$ (R = Sm and Eu) is shown in Figs. 6 and 7, respectively. For $Sm_2Ru_2O_7$, one sharp peak and another broad peak of the real part χ' susceptibilities are observed at 22 and 12 K, respectively (Fig. 6a). This sharp maximum in the χ' vs T curve corresponds to the cusp found at the same temperature in the dc susceptibility vs temperature curve (2). With decreasing frequency, the position of the peak in χ' shifts toward lower temperature and are sharper. The presence of a frequency-dependent maximum is often taken as a sign of either spin glass or superparamagnetic behavior. To distinguish between these possibilities, it is common to compute the quantity (6)

$$K = \frac{\Delta T_g}{T_g \Delta \ln(f)}, \qquad [1]$$

where T_g is the maximum in χ', f is the frequency, and Δ refers to differences between measurements at different frequencies. For spin glasses K is found to be of the order of 0.01, while for superparamagnets $K > 0.1$. For $Sm_2Ru_2O_7$, K is caluculated to be 0.001, which indicates that this compound is in the spin glass category. The imaginary part χ'' also exhibits two small anomalies with the inflection point of the χ'' vs T curve closely coinciding in temperature with the peak in the χ' curve.

Figure 6b shows the temperature dependence of the ac susceptibilities for $Sm_2Ru_2O_7$ in the temperature region between 120 and 130 K. The result is similar to the case for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$; i.e., both the dc susceptibility and the real part χ' of the ac susceptibility show a maximum at the same temperature in their susceptibility vs temperature curves, and the imaginary part χ'' of the ac susceptibility shows no anomaly in the ac susceptibility vs temperature curve.

Figure 7 shows the temperature dependence of the ac susceptibility for $Eu_2Ru_2O_7$ in the temperature range between 10 and 30 K. Both the real part χ' and the imaginary part χ'' of the susceptibilities show peaks at the same temperature, 23 K. This peak corresponds to the anomaly found in its dc susceptibility vs temperature curves (2). The peak in χ' shifts toward lower temperature with decreasing

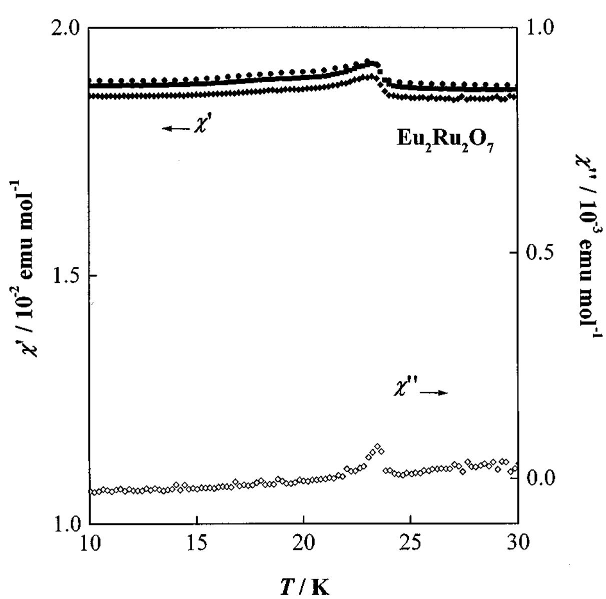

FIG. 7. Temperature dependence of ac susceptibilities for $Eu_2Ru_2O_7$. (●, ○) 80 Hz, (■, □) 888 Hz, (◆, ◇) 8888 Hz.

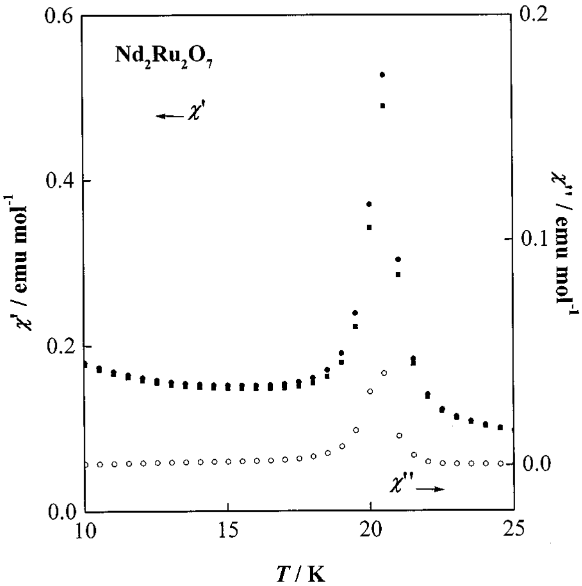

FIG. 8. Temperature dependence of ac susceptibilities for $Nd_2Ru_2O_7$. (■, □) 888 Hz, (◆, ◇) 8888 Hz.

frequency, as the case of $R = Sm$. For $Eu_2Ru_2O_7$, K is calculated to be 0.004 and the compound is in the spin glass category. The magnetic behavior for $Sm_2Ru_2O_7$ and $Eu_2Ru_2O_7$ at lower temperatures ($\sim$20 K) is considered to be the spin-glass type from two experimental results, i.e., the specific heat shows no anomaly even at transition temperatures and the ac susceptibility (both the real part and the imaginary part) is dependent on frequency. However, the transition found at 124 K for $R = Sm$ and at 118 K for $R = Eu$ seems to be not an ordinary spin-glass one.

Figure 8 shows the temperature dependence of the ac susceptibilities for $Nd_2Ru_2O_7$. A sharp peak is observed at 20 K for the real part χ' of the susceptibility. The peak in χ' shifts toward lower temperature with decreasing frequency and the imaginary part χ'' exhibits a small anomaly at the same temperature with the peak in χ', as the case of $R = Sm$ and Eu. These experimental results for $Nd_2Ru_2O_7$ suggest that the spin glass transition occurred at 20 K, although the jump of the specific heat is observed at the same temperature. The value of K for $Nd_2Ru_2O_7$ is calculated to be 0.001, which also indicates that this compound is in the spin glass category.

Table 1 summarizes the experimental results of the dc and ac magnetic susceptibility and specific heat measurements for $R_2Ru_2O_7$ (R = Y, Pr, Nd, Sm, Eu, and Lu).

λ-Type specific heat anomalies have been observed at 77, 78, 162, 143, 124, and 118 K for $R_2Ru_2O_7$ (R = Y, Lu, Pr, Nd, Sm, and Eu, respectively). These temperatures are consistent with the magnetic transition temperatures found in their magnetic susceptibilities vs temperature curves. In the real part of the ac susceptibilities, small cusps are observed at the same temperatures with the magnetic transition temperatures, but the imaginary part of the susceptibility show no anomaly at the corresponding temperatures. For $Sm_2Ru_2O_7$ and $Eu_2Ru_2O_7$, no specific heat anomaly has been found at lower temperatures, although magnetic anomaly was observed at ca. 20 K in their dc susceptibility vs temperature curves. Both the real and the imaginary parts of ac susceptibilities show anomaly at ca. 20 K and this temperature decreases with decreasing frequency. These

TABLE 1
Summary of the Experimental Results of Magnetic Susceptibility and Specific Heat Measurements for $R_2Ru_2O_7$ (R = Y, Pr, Nd, Sm, Eu, and Lu)

			ac Susceptibility	
	dc Susceptibility χ^a	Specific heat C^b	Real part χ'	Imaginary part χ''
$Y_2Ru_2O_7$	80	77 (λ-type peak)	78 (cusp, independent of frequency)	No anomaly
$Lu_2Ru_2O_7$	80	78 (λ-type peak)	80 (cusp, independent of frequency)	No anomaly
$Pr_2Ru_2O_7$	165	162 (λ-type peak)	—	—
	—	2 (Schottky-type)	—	—
$Nd_2Ru_2O_7$	145	143 (λ-type peak)	—	—
	20 (cusp)	20 (λ-type peak)	20 (cusp, dependent on frequency)	20 (cusp, dependent on frequency)
$Sm_2Ru_2O_7$	125	124 (λ-type peak)	128 (cusp, independent of frequency)	(No anomaly)
	20	(No anomaly)	22, 12 (cusp, dependent on frequency)	22, 12 (cusp, dependent on frequency)
$Eu_2Ru_2O_7$	120	118 (λ-type peak)	118 (cusp, independent of frequency)	(No anomaly)
	20 (cusp)	(No anomaly)	23 (cusp, dependent on frequency)	23 (cusp, dependent on frequency)

Note. The results on these dc susceptibility measurements have been published in Ref. (1) and (2).

[a] These are the temperatures (in K) at which dc magnetic susceptibilities show maxima. Therefore, these temperatures are higher than the magnetic transition temperatures by ca. 2 K.

[b] Peak temperatures (in K) at which the λ-type anomalies are observed in the specific heat vs temperature curves.

results strongly indicate that the transition observed at ca. 20 K is the spin-glass one.

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