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BRIEF COMMUNICATION

Magnetic Properties of Ruthenium Pyrochlores $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$

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Magnetic susceptibility and magnetic hysteresis measurements were performed for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$, which show magnetic transitions at 80 and 85 K, respectively. Below the transition temperatures, there is a large difference in the temperature dependence of the magnetization measured between under zero-field cooled condition and under field-cooled condition, but no magnetic hysteresis has been observed. These results suggest that below the temperatures, both $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ transform to a spin-glass state which is independent of the applied magnetic field. © 1999 Academic Press

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 the 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 behavior 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 $A_2M_2O_7$ formulation 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). However, little is known about the properties of $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$. $Y_2Ru_2O_7$ is paramagnetic down to 2.0 K as determined by magnetic susceptibility measurement (13, 14); nothing is known about the properties of $Lu_2Ru_2O_7$. Since both the Y^{3+} ion and the Lu^{3+} ion are diamagnetic, the magnetic properties of $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ should be attributable to the properties of the Ru^{4+} ions in the pyrochlore structure.

In this study, we will report the synthesis, the crystal structure determination, and magnetic properties of $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$.

EXPERIMENTAL

Sample Preparation

As starting materials, rare earth sesquioxides A_2O_3 (A = Y, Lu) and ruthenium dioxide RuO_2 were used. The A_2O_3 and RuO_2 were weighed in the correct ratios, intimately mixed, and heated in air at 900°C for 6 h. After cooling to room temperature, the samples were crushed into powder, reground, repressed into pellets, and then reheated at 1200°C for 48 h, with several intermediate regrindings. Both samples were prepared twice in a separate run and were reproducible in their magnetic properties.

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 the Rietveld program RIETAN (15).

Magnetic Measurements

Magnetic susceptibility and magnetization measurements were performed with a SQUID magnetometer (Quantum Design MPMS model). The temperature dependence of the

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magnetic susceptibilities was investigated under zero-field-cooled condition (ZFC) and field-cooled condition (FC). The former was measured in a residual magnetization mode on heating the sample to 300 K at 1000 G after zero-field cooling to 2.0 K. The latter was measured on cooling the sample from 300 to 2.0 K at 1000 G. These magnetic susceptibility measurements were also performed while applying lower magnetic fields (50, 100, and 500 G). The field dependence of the magnetization was measured at 5 K by changing the applied magnetic field between $-50{,}000$ and 50,000 G.

RESULTS AND DISCUSSION

X-ray diffraction analyses on the desired pyrochlore-type compounds $A_2Ru_2O_7$ (A = Y, Lu) showed that very small amounts of impurities remained in the compounds; these were unreacted starting materials. Since these are diamagnetic or very weakly paramagnetic (Pauli paramagnetic), the effect of such impurities on the magnetic properties of the pyrochlore-type compounds is negligible. The lattice parameters of $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ are $a_0 = 10.141$ and 10.055 Å, respectively, in excellent agreements with those reported by other workers (16, 17). The lattice parameter of $Y_2Ru_2O_7$ is larger than that of $Lu_2Ru_2O_7$, consistent with the fact that the ionic radius of the Y^{3+} ion is larger than that of the Lu^{3+} ion (18).

Figure 1 shows the temperature dependence of the susceptibilities; $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ show magnetic transitions at 80 and 85 K, respectively. Our experimental results are quite different from those of previous workers (13) who found that $Y_2Ru_2O_7$ remains paramagnetic between 2.0 K and room temperature. There is no report on the magnetic properties for $Lu_2Ru_2O_7$. The magnetic susceptibilities measured under ZFC and under FC show a different temperature dependence for both $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$. The ZFC susceptibilities decrease with decreasing temperature, while the FC susceptibilities increase with decreasing temperature. The most striking feature is the divergence of the ZFC and FC magnetic susceptibilities below the transition temperature. The magnetic behavior below 80 K indicates the onset of magnetic ordering between ruthenium ions at short distances and the existence of frustration. The high transition temperatures and the very large differences between the ZFC susceptibility and FC susceptibility indicate the existence of a very strong interaction between ruthenium ions. Figure 2 shows the temperature dependence of the susceptibility for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ in various applied magnetic fields. No significant change in transition temperature or in the magnetic susceptibility-temperature behavior with the applied magnetic fields are observed.

We now discuss the origin for the divergence of the ZFC and FC magnetic susceptibilities below the transition temperature. We considered the possibility that weak ferromagnetism might be responsible for the very large divergence between ZFC and FC susceptibilities. To check on this, magnetic hysteresis measurements (field dependence of the magnetization) were performed on $Y_2Ru_2O_7$. The results are shown in Fig. 3. No magnetic hysteresis was observed, but the measurements of FC magnetization differ from those of the ZFC magnetization. In the case of field cooling, we report one important observation: remanent magnetization exists in zero magnetic field, unlike the case of zero-field cooling, which leads to the spin-frozen state of the magnetic elements (19, 20). Figure 4 shows the results of residual magnetization measurements for $Y_2Ru_2O_7$. We performed two kinds of measurements; the first (A) was measured on heating the sample to 100 K after zero-field cooling to 2.0 K, applying a magnetic field of 50,000 G, and then reducing it to zero. The other (B) was measured on heating the sample to 100 K after cooling in a 50,000 G and then reducing the magnetic field to zero. The residual magnetization measured by method (A) differs greatly from that obtained by method (B). This shows that there is no

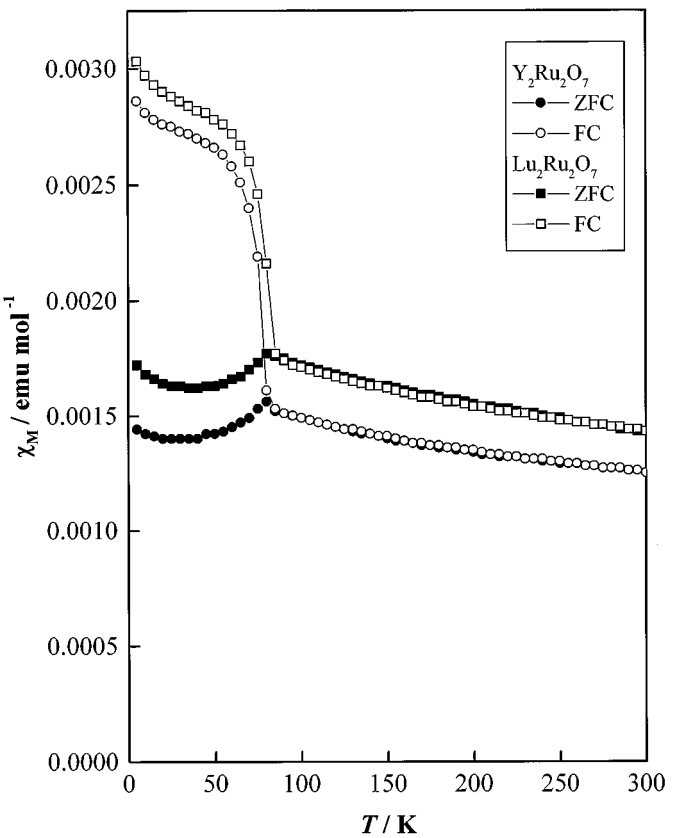

FIG. 1. Temperature dependence of the susceptibilities for $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$. The applied magnetic field is 1,000 G. Filled symbols (●, ■) correspond to ZFC susceptibilities and open symbols (○, □) correspond to FC susceptibilities.

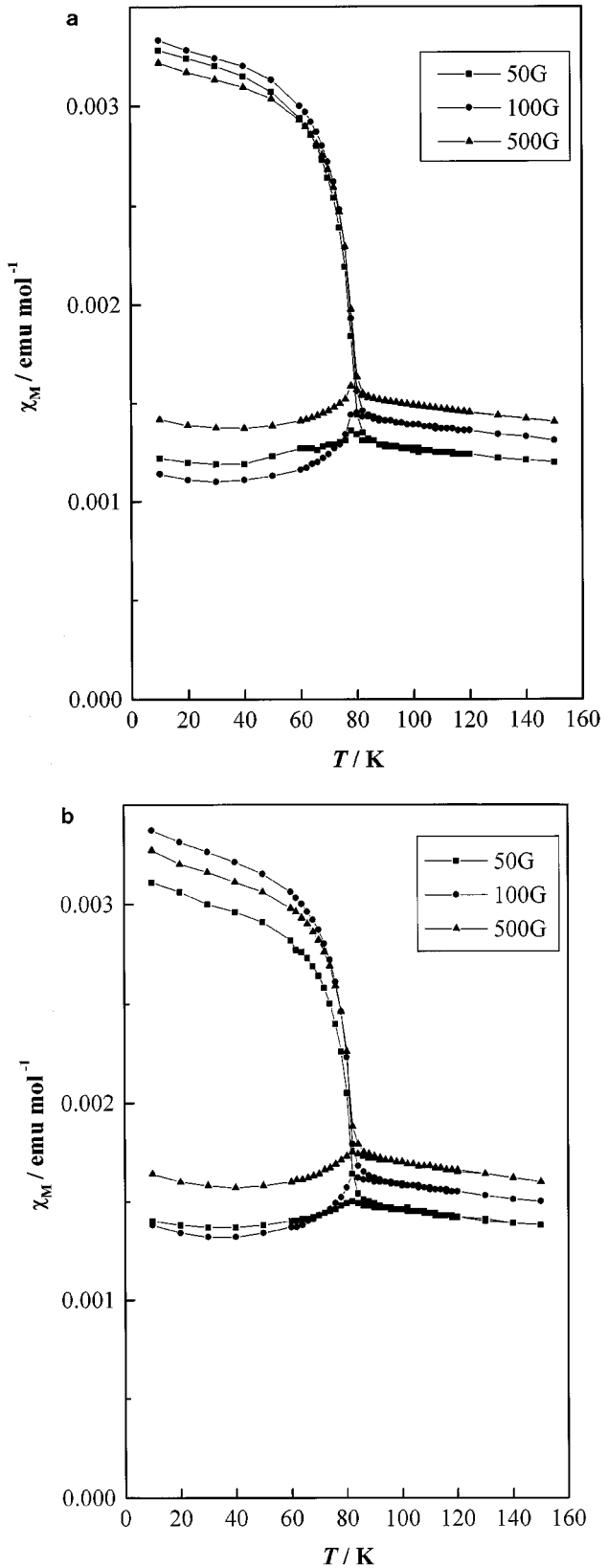

FIG. 2. Susceptibilities at low temperatures for (a) $Y_2Ru_2O_7$ and (b) $Lu_2Ru_2O_7$. The applied magnetic field are 50, 100, and 500 G.

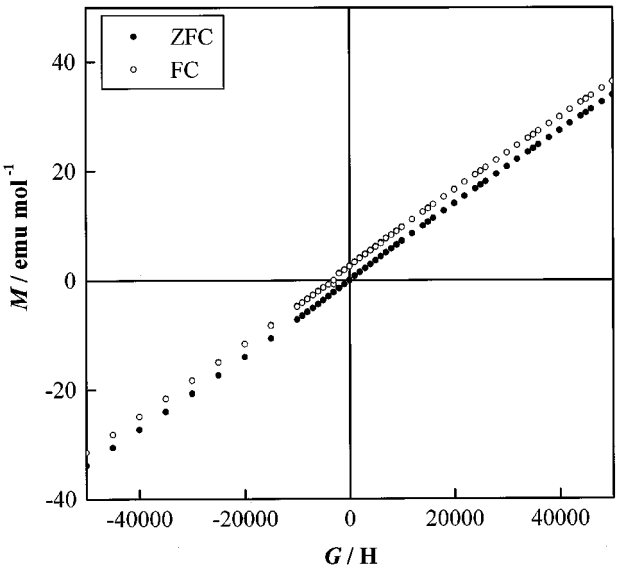

FIG. 3. Magnetic hysteresis curves (field-dependence of the magnetization) for $Y_2Ru_2O_7$ at 5 K.

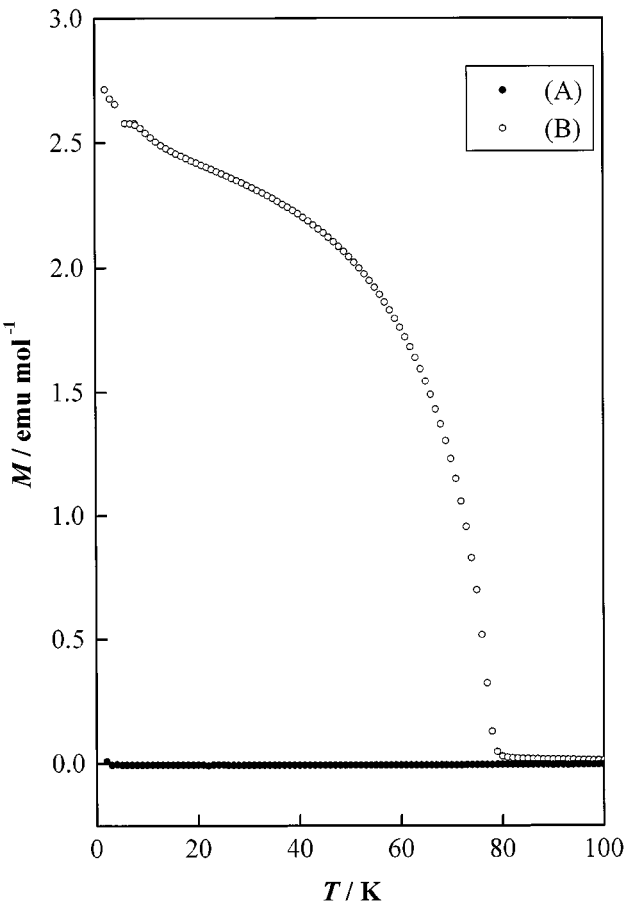

FIG. 4. Temperature dependence of the residual magnetization for $Y_2Ru_2O_7$. (A), measured on heating the sample after zero-field cooling, applying a 50,000 G field, and then reducing it to zero; (B), measured on heating the sample after cooling in a 50,000 G field and then reducing the magnetic field to zero.

possibility of a contribution of the weak ferromagnetism exists in $Y_2Ru_2O_7$, as checked by both the magnetic hysteresis and residual magnetization measurements.

The present experimental results, especially the results on the magnetic hysteresis measurements shown in Fig. 3, suggest that below the transition temperature both $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ transform to a spin-glass state which is independent of the applied magnetic field. The unusual magnetic properties of these $Y_2Ru_2O_7$ and $Lu_2Ru_2O_7$ may be related to the complexity of their pyrochlore-type crystal structures.

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