Spin Glass Behavior in Metallic Pyrochlore Ruthenate Ca$_2$Ru$_2$O$_7$

T. Taniguchi$^1$, T. Munenaka$^2$ and H. Sato$^2$

$^1$ Graduate School of Science, Osaka University, Osaka 560-0043, Japan
$^2$ Department of Physics, Chuo University, Tokyo 112-8551, Japan
E-mail: ttani@ltfridge.ess.sci.osaka-u.ac.jp
E-mail: hirohiko@phys.chuo-u.ac.jp

Abstract. Spin glass properties of a novel ruthenate, Ca$_2$Ru$_2$O$_7$, were studied by precise magnetization measurements. The effective moment per Ru atom is only 0.25 $\mu_B$, which is one decade smaller than that expected from a localized spin model with $S = 3/2$ for Ru$^{5+}$. In spite of the small moment, a spin glass transition occurs at $T_g = 25.0$ K, and the nonlinear susceptibility $\chi_{nl}(\approx \chi^2)$ diverges negatively at $T_g$. The value of the critical exponent $\delta$ can be estimated as $\delta = 3.7$ from the magnetic field dependence of $\chi_{nl}$ at $T_g$, which is compared to those of other pyrochlore spin glasses and the canonical spin glasses.

1. Introduction
Geometric frustration arises in materials containing antiferromagnetically coupled magnetic moments which reside on geometrical units, such as triangles and tetrahedra, that inhibit the formation of a collinear magnetically ordered state. Systems of classical Heisenberg spins residing on lattices of corner-sharing triangles or tetrahedra and antiferromagnetically coupled via nearest-neighbor exchange constitute particularly interesting cases of highly frustrated antiferromagnets. Here, theory and numerical work [1, 2, 3] show that these systems do not order down to zero temperature. Since, even for classical spins, these systems have such a small tendency to order, they are excellent candidates for displaying exotic disordered ground states. However, and perhaps most interestingly, experiments show that some nominally perfect (i.e., disorder-free) [4] pyrochlore antiferromagnetic lattices of corner-sharing tetrahedra exhibit a spin glass transition at some temperature $T_g$ [5], below which they develop magnetic irreversibilities and longtime magnetic relaxation similar to what is found in conventional randomly frustrated spin glasses such as CuMn, EuSrS, and CdMnTe [6].

Two important questions arise: Firstly, what is the microscopic origin of the spin glass behavior in pyrochlore antiferromagnets? Is it due to the yet undetected microscopic disorder inherent to any real material, or is it intrinsic to the idealized perfect material? Secondly, irrespective of the origin of the spin glass behavior, one would like to know if the spin freezing is strictly dynamical (i.e., where the system’s relaxation time exceeds the time scale set by the experimental probe), or is it due to an underlying thermodynamic transition characterized by a truly divergent spin glass correlation length and time scale as is believed to occur in conventional disordered spin glasses? A divergence of the nonlinear susceptibility at $T_g$ were reported in the geometrically frustrated spin glass pyrochlore Y$_2$Mo$_2$O$_7$ and the critical exponents of the spin
glass transition were obtained as $\gamma \approx 2.7$, $\beta \approx 0.8$ and $\delta \approx 4.7$ [7]. A new pyrochlore ruthenate Ca$_2$Ru$_2$O$_7$ has recently been discovered [8]. Bulk magnetic measurements on Ca$_2$Ru$_2$O$_7$ suggest that a spin glass transition occurs at $T \approx 23$ K. It is interesting to compare the critical phenomena of the spin glass transition between two systems with the different electronic states; Y$_2$Mo$_2$O$_7$, an insulator and Ca$_2$Ru$_2$O$_7$, a metallic oxide. Is the universality class of spin glass transition of Ca$_2$Ru$_2$O$_7$ the same as that of Y$_2$Mo$_2$O$_7$? To address these questions, we have measured the nonlinear magnetic susceptibility, $\chi_{nl}$, of the pyrochlore ruthenate Ca$_2$Ru$_2$O$_7$.

2. Experimental

Single crystals of Ca$_2$Ru$_2$O$_7$ were synthesized by a hydrothermal method. A mixture of RuO$_2$, obtained by oxidizing Ru metal, CaO and 30 % H$_2$O$_2$ solution was encapsulated in a gold tube. Then, it was kept in an autoclave under 150 MPa hydrostatic pressure at 600 °C for 3 days. The obtained materials were black crystals with an octahedral shape. The typical dimensions of the crystals are $0.1 \times 0.1 \times 0.1$ mm$^3$. The chemical composition was determined using an energy dispersive X-ray spectrometer (EDS) installed on a scanning electron microscope. The crystal structure was analyzed using a single crystal and an imaging-plate X-ray diffractometer (Rigaku, R-Axis RAPID), in which Mo-K$\alpha$ radiation was generated using an X-ray tube and monochromized using graphite. We also used a powder X-ray diffractometer to check whether there was any contamination due to impurity phases. These analysis on a single crystal revealed that this material crystallizes in a pyrochlore structure with a lattice parameter, $a = 10.197$ Å. The magnetization was measured using a commercial SQUID (Quantum Design, MPMS) magnetometer. In the measurement, approximately 40 mg of nonoriented single crystals were used.

3. Results and discussion

Figure 1 shows the temperature dependence of the magnetic susceptibility $M/H$ of Ca$_2$Ru$_2$O$_7$. The zero field-cooled (ZFC) susceptibility shows a sharp cusp at 25.0 K, and below the temperature the field-cooled (FC) susceptibility is apart from the ZFC one. Above 30 K, $M/H$ can be well fitted as follows:

$$M/H = \chi_{const} + \frac{C}{T - \Theta},$$

where $\chi_{const}$, $C$ and $\Theta$ are a constant term independent of temperature, the Curie constant and the Weiss temperature respectively. The best-fitted values are $\chi_{const} = 2.4 \times 10^{-4}$ emu/mol Ru, $C = 7.84 \times 10^{-3}$ emu K/mol Ru and $\Theta = -5.0$ K. These values are almost the same as those
reported previously. The effective moment per Ru atom is determined to be 0.25\(\mu_B\) from the fitting result shown as a solid line in Fig. 1, which is one decade smaller than that of free Ru\(^{3+}\) ion. We should note that the spin glass transition temperature becomes so high in such a small moment system.

To determine whether or not a true thermodynamic spin glass transition occurs around \(T_g \approx 25\) K in \(\text{Ca}_2\text{Ru}_2\text{O}_7\), we have measured the nonlinear susceptibility coefficient, \(\chi_2(T)\), which is expected to show a power-law critical divergence at \(T_g\):

\[
\chi_2 \sim \varepsilon^{-\gamma}
\]

with \(\varepsilon \equiv T/T_g - 1\). \(\chi_2\) is extracted from the temperature \(T\) and field \(H\) dependence of the magnetization, \(M = \chi_0(T)H + \chi_2(T)H^2 + \chi_4(T)H^4 + \cdots\), where \(\chi_0\) is the linear susceptibility and \(\chi_2, \chi_4, \cdots\) are nonlinear susceptibilities. Hence, the temperature dependence of \(\chi_2\) allows a determination of \(T_g\) and \(\gamma\). In fact, all the nonlinear terms \(\chi_{2n}\) with \(n > 1\) must diverge at \(T_g\), since both \(\chi_2\) and \(\chi_{2n}\) are finite quantities. It is therefore convenient to define a net nonlinear susceptibility, \(\chi_{nl}\), as \(\chi_{nl} \equiv \chi_0 - M/H\). Right at \(T_g\), \(\chi_{nl}\) has a power-law dependence on \(H\):

\[
\chi_{nl}(T = T_g, H) \sim H^{2/\delta}
\]

where \(\delta\) is a second independent static critical exponent characterizing the spin glass transition.

We show the net nonlinear susceptibility, \(\chi_{nl}(T, H)\), with \(\chi_0\) extracted from the \(M(T, H)/H\), as a function of \(H^2\) for few temperatures above \(T_g\) in Fig. 2 (a). We notice that \(\chi_{nl}\) is proportional to \(H^2\) in the low field limit and the initial slope corresponds to \(\chi_2\). The absolute value of the initial slope quickly increases with approaching \(T_g\), but still remains at high temperatures \((T = 100, 300\) K\). These results emphasize the large increase of \(-\chi_{nl}\) upon approaching \(T_g\). A negative divergence of \(\chi_2\) at \(T_g\) is directly observed in the temperature dependence of \(\chi_2(T)\) shown in Fig. 2 (b). This behavior strongly suggests that the spin glass transition of \(\text{Ca}_2\text{Ru}_2\text{O}_7\) is intrinsic because \(\chi_2\) is directly connected to the order parameter of the spin glass phase with \(H^2\), and the divergence of \(\chi_2\) means a large fluctuation of the order parameter. The fluctuation is characterized by the critical exponent \(\gamma\), which was estimated as \(\gamma \approx 1\) with \(T_g = 25.0\) K from the temperature dependence of \(\chi_2(T)\). However, it should be noted that the value of \(\gamma\) contains the large experimental error because the value is sensitive to the subtraction of the constant term observed at high temperatures and the number of the data points is not sufficient to determine the precise value.

Figure 2. (a) Net nonlinear susceptibility, \(\chi_{nl} = \chi_0 - M/H\) vs \(H^2\) for the six temperatures indicated. (b) Temperature dependence of nonlinear susceptibility \(\chi_2\).
Figure 3 shows a log-log plot of $\chi_{nl}$ vs $H$ at $T = T_g (= 25.0 \, K)$. Two different regimes, corresponding to exponents $\delta = 3.7$ and $\delta = 6.7$, are observed in the low and high field limits. From the arguments about the critical region of the spin glass transition \[9, 10\], the value of $\delta$ should be determined in the low field limit. The critical phenomena of the spin glass transition have been extensively investigated in a wide class of spin glass systems. It is interesting to compare our results for Ca$_2$Ru$_2$O$_7$ with those for the canonical spin glasses and the insulator pyrochlore Y$_2$Mo$_2$O$_7$. The value of $\delta = 3.7$ determined on Ca$_2$Ru$_2$O$_7$ is slightly larger than that of the canonical spin glass systems, $\delta = 3.1$, and quite different from that of Y$_2$Mo$_2$O$_7$, $\delta = 4.7$. It should be noted that the value of $\delta$ is more reliable than that of $\gamma$, since the $\chi_0$ includes the contribution of the constant term $\chi_{const}$ in the field dependence measurements at the fixed temperature.

![Figure 3](image.png)

**Figure 3.** The log-log plot of $\chi_{nl}(T = T_g, H) \sim H^{2/\delta}$ with the value of $\delta = 3.7$ in the low field limit and $\delta = 6.7$ in the high field limit.

In summary, the temperature dependence of $\chi_2(T)$, which represents the spin glass susceptibility, shows a negative divergence at $T_g$, and it strongly suggests that the spin glass transition is intrinsic in the system. The value of the critical exponent $\delta$ can be estimated as $\delta = 3.7$ from the magnetic field dependence of $\chi_{nl}$ at $T_g$. The value is slightly larger than that of canonical spin glass systems but quite different from that of Y$_2$Mo$_2$O$_7$, which means the spin glass transition of the system seems to belong to the same universality class of the canonical spin glass. In order to determine the critical exponents precisely, a full scaling analysis is required.

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**References**

[1] Villain J, 1978 Z. Phys. B 33 31
[2] Reimers J N et al. 1991 Phys. Rev. B 43 865
[3] Chalker J T et al. 1992 Phys. Rev. Lett. 68 855
[4] Greedan J E et al. 1986 Solid State Commun. 59 895
[5] Reimers J N et al. 1991 Phys. Rev. B 43 3387
[6] Binder K and Young A P 1986 Rev. Mod. Phys. 58 801
[7] Gingras M J P, et al. 1997 Phys. Rev. Lett. 78 947
[8] Munenaka T and Sato H, 2006 J. Phys. Soc. Jpn. 75 103801
[9] Bouchiat H 1986 J. Phys. (Paris) 47 71
[10] Taniguchi T and Miyako Y 1988 J. Phys. Soc. Jpn. 57 3520