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SEARCH FOR THE QUANTUM SPIN LIQUID STATE IN PYROCHLORE OXIDES*

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We have investigated a pyrochlore Mott insulator $Y_2Ir_2O_7$ with an expectation that $5d^5$ electrons of Ir ions in the t_{2g} orbitals give rise to an $S = 1/2$ Heisenberg system and form a quantum spin-liquid state. However, it exhibits spin–glass ordering below about 170 K. Such spin-glass ordering is also observed in its isomorphs $Y_2Mo_2O_7$ and $Y_2Ru_2O_7$ with $S = 1$.

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Quantum spin-liquid (QSL) state is one of the important subjects of the research on the geometrically frustrated systems [1]. In this state all the spins form only spin-singlet pairs, which give rise to macroscopic degeneracy of the ground state, namely a residual entropy. The existence of the QSL state has been theoretically expected for the Heisenberg antiferromagnetic (AF) spins on the pyrochlore lattice [2]. However, there are few candidates of the real materials in which the QSL state is indeed realized.

Recently pyrochlore iridates, $R_2Ir_2O_7$ (R = Y and lanthanides), have provided additional research interests in this respect [3–5]. These materials were reported as early as about 30 years ago but were little studied [6]. Kennedy *et al.* [7] studied the crystal structure of the materials, but did not report the low-temperature properties, which are essential for the characterization of the frustrated magnetic systems.

The magnetic frustration arises because of the pyrochlore structure in which R and Ir sub-lattices form individual networks of linked tetrahedra. Systematic variations of the physical properties have been investigated by

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changing the elements of the R site [3]. Furthermore, one may expect that each Ir ion has a quantum spin $S = 1/2$ if the five $5d$ electrons in the t_{2g} orbitals are localized in the presence of strong electronic correlation. Although the QSL state is theoretically expected for antiferromagnetic Heisenberg pyrochlore magnet [2], there have been few candidates of the actual materials studied up to now. These urge us to study the $S = 1/2$ pyrochlore system, pyrochlore iridates.

Of the pyrochlore iridates, $Y_2Ir_2O_7$ serves as a reference material, since it does not possess a magnetic rare-earth element on the R site and its physical properties are comparable with those of its isomorphs $Y_2Mo_2O_7$ [8] and $Y_2Ru_2O_7$ [9], based on $S = 1$.

$Y_2Ir_2O_7$ exhibits non-metallic behavior down to 4.2 K and exhibits quite a small ferromagnetic (FM) component below $T_{\mathrm{m}} = 170$ K, though it has not been well understood whether such FM component is intrinsic or not [3,4]. In spite of the non-metallic behavior, it has been reported by Taira *et al.* [4] that the γ is finite, 4.1(3) mJ/K^{2}mol-Ir, suggesting the existence of the Fermi surface. We will discuss the origins of the FM component and the finite γ of $Y_2Ir_2O_7$.

We used polycrystals synthesized by the conventional solid-state-reaction method [3]. We measured the resistivity by a standard four-probe method below 300 K and the specific heat by a relaxation method between 1.8 and 300 K (Quantum Design, PPMS). We investigated the dc magnetization with a SQUID magnetometer (Quantum Design, MPMS$_{5\mathrm{S}}$) between 1.8 and 350 K. The crystal structure is cubic with the lattice parameter at room temperature $a = 10.176(1)$ Å.

In Fig. 1, we plot the dc magnetic susceptibility $M(T)/H \equiv \chi(T)$ ($\mu_0 H = 1$ T). Very small FM component, amounting to 4×10^{-3} of the saturated moment of $S = 1/2$ spins, is observed. The T_{m} of $Y_2Ir_2O_7$ is about 170 K consistent with the value previously reported by us [3] and by Taira *et al* [4]. We obtained the effective spin $S_{\mathrm{eff}} = 0.07(1)$ from the Curie–Weiss fitting

$$(\chi(T) = \chi_0 + \frac{4\mu_{\mathrm{B}}^2 S_{\mathrm{eff}}(S_{\mathrm{eff}}+1)}{3k_{\mathrm{B}}(T-\theta_{\mathrm{CW}})}$$

for $Y_2Ir_2O_7$ above T_{m}. It corresponds to only 14(2)% of the expected spin $S = 1/2$.

In the inset of Fig. 1, we show specific heat of $Y_2Ir_2O_7$ between 100 and 200 K. No peak was observed at around T_{m}, though the slope of C *vs* T changes at around 150 K. The linear fittings between 100 and 145 K and between 170 and 200 K, represented by the two solid lines in the inset, cross at 150 K. This temperature reasonably corresponds to the T_{m} in $\chi(T)$. The

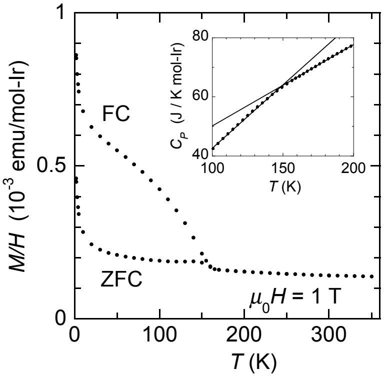

Fig. 1. Magnetic susceptibility of $Y_2Ir_2O_7$. Data for both zero-field-cooling (ZFC) and field-cooling (FC) sequences are shown. Specific heat of $Y_2Ir_2O_7$ are shown in the inset. Two solid lines denote the linear fittings between 100 and 145 K and between 170 and 200 K.

small magnetic moment of $Y_2Ir_2O_7$ below T_{m} may be due to either spin-glass ordering or canted antiferromagnetic ordering. Since only the slope change but no peak was observed in the specific heat, the FM component is ascribable to spin–glass ordering as previously reported in other pyrochlores, such as $Y_2Mo_2O_7$ [8] and $Y_2Ru_2O_7$ [9].

We should note that an additional steep increase of magnetization was observed with decreasing temperature below about 15 K. Since no change in $\rho(T)$ was observed below this temperature, the increase is attributable to magnetic impurities or localized Ir spins at grain boundaries.

In Fig. 2, we plot the specific heat divided by temperature, $C_P(T)/T$, against T^2. Solid line denotes the quadratic fitting, $C_P/T = \gamma + \beta T^2$, between 14 and 20 K. Below 14 K, it is difficult to perform a valid quadratic

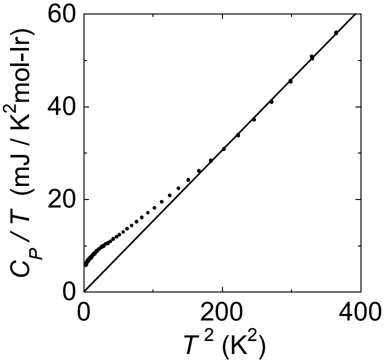

Fig. 2. Specific heat of $Y_2Ir_2O_7$. Solid line denotes the quadratic fitting between 14 and 20 K.

fitting because of additional increase of C_P/T with decreasing T [10]. This increase cannot be explained in terms of the localization effect, since in such a case C_P/T should exhibit linear behavior (the Debye T^3 term) with the same slope and the same finite intercept γ at least up to 20 K. We speculate that the origin of the increase is attributable to a magnetic contribution, since it appears to correspond to the steep increase of $\chi(T)$ below 15 K.

Although C_P/T of $Y_2Ir_2O_7$ at 1.8 K is 5.8(2) mJ/K^{2}mol-Ir, we may consider that the γ, which is equal to 0.0(5) mJ/K^{2}mol-Ir, is the intrinsic electronic specific heat coefficient. This value strongly suggests that $Y_2Ir_2O_7$ is a Mott insulator.

In summary, we have revealed that $Y_2Ir_2O_7$ is a Mott insulator. Although it does not exhibit the QSL behavior, spin-glass ordering occurs below 170 K reflecting the geometrical frustration of the pyrochlore structure as previously reported in $Y_2Mo_2O_7$ and $Y_2Ru_2O_7$.

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