Filling control of the pyrochlore oxide

\textit{Y}_2\textit{Ir}_2\textit{O}_7

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Recently pyrochlore iridates, \textit{R}_2\textit{Ir}_2\textit{O}_7 (\textit{R} = \text{Y} and lanthanides), have provided additional research interests in geometrically frustrated magnetic systems. These materials were reported as early as about 30 years ago but were little studied \textsuperscript{4,5} until Kennedy \textit{et al.}\textsuperscript{6} studied the crystal structure of the materials, but they have not reported 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 \textit{R} and \text{Ir} sub-lattices form individual networks of linked tetrahedra. Systematic variations of the physical properties have been investigated by changing the elements of the \textit{R} site.\textsuperscript{4,5} Furthermore, one may expect that each \text{Ir} ion has a quantum spin $S = 1/2$ if the $5d$ electrons in the $t_{2g}$ orbitals are localized in the presence of strong electron correlation. Although a quantum spin liquid state is theoretically expected for antiferromagnetic Heisenberg pyrochlore magnets, there have been few candidates of the actual materials studied up to now. Besides, Fujimoto \textit{et al.}\textsuperscript{7} theoretically showed for a hole-doped pyrochlore Mott-insulator based on an $s$-electron system that the electronic specific-heat coefficient $\gamma$ exhibits a divergent behavior near the boundary of metal-insulator transition. These urge us to study the $S = 1/2$ pyrochlore system, pyrochlore iridates.

Of the pyrochlore iridates, \textit{Y}_2\textit{Ir}_2\textit{O}_7 serves as a reference material, since it does not possess a magnetic rare-earth element on the \textit{R} site and its physical properties are comparable with those of its isomorphs \textit{Y}_2\textit{Mo}_2\textit{O}_7 and \textit{Y}_2\textit{Ru}_2\textit{O}_7 based on $S = 1$.

\textit{Y}_2\textit{Ir}_2\textit{O}_7 exhibits non-metallic behavior down to 4.2 K and exhibits quite a small ferromagnetic (FM) component below $T_m = 170$ K, though it has not been well understood whether such FM component is intrinsic or not.\textsuperscript{8} In spite of the non-metallic behavior, it has been reported by Taira \textit{et al.}\textsuperscript{9} that the $\gamma$ is finite, 4.1(3) mJ/K$^2$mol-Ir, suggesting the existence of the Fermi surface. We will discuss the origins of the finite $\gamma$ and the FM component of \textit{Y}_2\textit{Ir}_2\textit{O}_7. It is vital to investigate the filling control of \textit{Y}_2\textit{Ir}_2\textit{O}_7 in order to search for the metallic phase adjacent to the strongly correlated nonmetallic phase. We succeeded in synthesizing hole-doped material, namely \textit{Y}_{2-x}\textit{Ca}_x\textit{Ir}_2\textit{O}_7 ($x = 0.2$, 0.3, 0.4 and 0.6). As the main purpose of this note, we will show the metal/non-metal (M/NM) crossover and the enhancement of the $\gamma$ in \textit{Y}_{2-x}\textit{Ca}_x\textit{Ir}_2\textit{O}_7.

We used polycrystals synthesized by the conventional solid-state-reaction method. \textsuperscript{10} We measured the resistivity by a standard four-probe method below 1.8 and 300 K (Quantum Design, PPMS). We investigated the dc magnetization with a SQUID magnetometer (Quantum Design, MPMS5S) between 1.8 and 350 K.

![Fig. 1. Resistivity of \textit{Y}_{2-x}\textit{Ca}_x\textit{Ir}_2\textit{O}_7.](image)

The lattice parameters at room temperature depend little on $x$ ($a = 10.184(2)$Å, cubic) except for $x = 0.0$ ($a = 10.176(1)$Å, cubic). We note that transport properties at room temperature also change from non-metallic to metallic between $x = 0.0$ and 0.2.

In Fig. 1, we plot the resistivities of \textit{Y}_{2-x}\textit{Ca}_x\textit{Ir}_2\textit{O}_7. \textit{Y}_2\textit{Ir}_2\textit{O}_7 exhibits non-metallic behavior, as we previously reported.\textsuperscript{8} For $x = 0.2$, it exhibits metallic behavior down to about 120 K, and non-metallic behavior at lower temperature. For $x = 0.3, 0.4$ and 0.6, it exhibits metallic behavior at least down to 0.3 K; however, no sign of superconductivity has been observed.

In Fig. 2, we plot the dc magnetic susceptibilities $\chi(T) = \chi(x) (\mu_0H = 1$ T). Very small FM component, amounting to $4 \times 10^{-3}$ of the saturated moment of $S = 1/2$ spins, is observed for $x = 0.0$ ($T_m = 170$ K) and 0.2 ($T_m = 100$ K). The $T_m$ of \textit{Y}_2\textit{Ir}_2\textit{O}_7 is consistent with the value previously reported by us\textsuperscript{10} and by Taira \textit{et al.}\textsuperscript{9} The FM component was not observed above $x = 0.3$. Thus, the magnetic ground state appears to be correlated with non-metallic ground state. We obtained the effective spin $S_{eff} = 0.07(1)$ from the Curie-Weiss fitting $\chi(T) = \chi_0 + \frac{\chi_m}{3k_B(T-\theta_{CW})}$ for \textit{Y}_2\textit{Ir}_2\textit{O}_7 above $T_m$. It corresponds to only 14(2)% of the expected spin $S = 1/2$.

Small magnetic moment of \textit{Y}_2\textit{Ir}_2\textit{O}_7 below $T_m$ may be due to either spin-glass ordering or canted antiferromagnetic ordering. Since no anomaly was observed at around $T_m$ in specific heat (data not shown), the FM component is attributable to spin-glass ordering as previously reported in other pyrochlores, such as \textit{Y}_2\textit{Mo}_2\textit{O}_7 and...
Y$_2$Ru$_2$O$_7$.

We should note that an additional steep increase of magnetization was observed for all the materials 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 Ir spins at grain boundaries.

In Fig. 2, magnetic susceptibilities of Y$_{2-x}$Ca$_x$Ir$_2$O$_7$. Solid symbols denote the data obtained after field-cooling. Open symbols denote the data obtained after zero-field-cooling.

In Fig. 3, we plot the specific heat divided by temperature, $C_p(T)/T$, against $T^2$. Solid line for $x = 0.0$ 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 fitting because of additional increase of $C_P/T$ with decreasing $T$. 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 finite intercept $\gamma$ 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$_2$Ir$_2$O$_7$ at 1.8 K is 5.8(2) mJ/K$^2$mol-Ir, we may consider that the $\gamma$, which is equal to 0.0(5) mJ/K$^2$mol-Ir, is the intrinsic $\gamma$. This value strongly suggests that Y$_2$Ir$_2$O$_7$ is a Mott insulator.

In the inset of Fig. 3, we show the $\gamma$ against the substitution content $x$. The $\gamma$ is obtained from the quadratic fitting between 14 and 20 K. We note that the Debye temperature is $\Theta_D = 400(10)$ K and depends little on $x$. Once additional holes are introduced into the half-filled $t_{2g}$ band, the finite density of states at the Fermi level appears. The $\gamma$ for $x = 0.2$ is 8.1(5) mJ/K$^2$mol-Ir much greater than the value, 1(1) mJ/K$^2$mol-Ir, for the corresponding material Y$_{1.8}$Bi$_{0.2}$Ru$_2$O$_7$. With increasing $x$ across the M/NM boundary, $\gamma$ nearly monotonically increases without clear divergent behavior. This is in contrast with the behavior in Y$_{2-x}$Bi$_x$Ru$_2$O$_7$, for which $\gamma$ takes a sharp maximum at the metal-insulator boundary. In order to explain the apparent discrepancy between our results and the theory based on an $s$-electron, we should take into account of the role of 5$d$ electrons, which give rise to more complicated band structure compared with that of $s$ electrons.

In summary, we have revealed that Y$_2$Ir$_2$O$_7$ is a Mott insulator. We have also shown that the density of states at the Fermi level rapidly changes with $x$ by the filling control of Y$_2$Ir$_2$O$_7$. The magnetic ground state appears to occur concomitantly with non-metallic state.

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