Structural, Magnetic, and Electrical Properties in the Metallic Pyrochlore $\text{Pr}_{2+x}\text{Ir}_{2-x}\text{O}_{7+\delta}$

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Abstract. $\text{Pr}_2\text{Ir}_2\text{O}_7$ is the metallic pyrochlore magnet which has been revealed to form a spin liquid phase by recent studies. Here we report results of structural, magnetic, and electrical transport properties of a newly synthesized polycrystalline sample of $\text{Pr}_2\text{Ir}_2\text{O}_7$. Our powder x-ray diffraction indicates the sample to be a single pyrochlore phase with a "Pr-stuffing" into the Ir site. The resistivity measurement suggests a phase transition into some sort of ordered phase, in contrast to the previous report. We discuss the possible origin of the phase transition.

1. Introduction
The pyrochlore magnets $A_2B_2O_7$, in which both $A$ and $B$ sites individually form a pyrochlore lattice [1], have been recognized as the fascinating venue where novel magnetic states can appear as a result of their geometrical frustration [2, 3]. Among them, much attention has been recently devoted to the pyrochlore $\text{Pr}_2\text{Ir}_2\text{O}_7$, a rare example of a metallic frustrated spin system [4-9]. In this compound, $\text{Pr}^{3+}$ and $\text{Ir}^{4+}$ ions carry the localized frustrated magnetism and conduction electrons, respectively, providing a unique opportunity to study the coupling between magnetism and conduction electrons. Despite relatively large negative Weiss temperature $\approx -20$ K (antiferromagnetic), no indication of magnetic long-range order has been observed at least down to $T_f = 110$ mK, where a partial spin freezing was found [5]. Instead, the Kondo effect emerges and leads to a partial screening of the moment below 20 K [5]. Furthermore, a spontaneous Hall effect, observed in the spin liquid region without uniform magnetization, indicates that the underscreened moments form a “chiral spin liquid” phase that breaks macroscopic time reversal symmetry without magnetic dipole order [7].

In general, a spin liquid state is destabilized by an external perturbation such as magnetic field and chemical disorder, and, consequently, a novel ordered phase might appear. Here we have investigated structural, magnetic, and electrical transport properties of a newly synthesized polycrystalline sample of $\text{Pr}_2\text{Ir}_2\text{O}_7$. The resistivity data suggest a phase transition into some sort of ordered phase. An origin of the phase transition will be discussed.

2. Experimental
Polycrystalline samples of $\text{Pr}_2\text{Ir}_2\text{O}_7$ were prepared by the solid state reaction of the mixture of $\text{Pr}_6\text{O}_{11}$ and IrO$_2$ powders. The mixture was first heated at 1273 K in air for 2 days with one intermediate gliding and then heated at 1433 K in an evacuated silica tube for about 1 week with multiple intermediate gridings. These heating temperature are higher than the one for the previous study (below 1223 K) [4]. A powder X-ray diffraction data was collected on a Rigaku RINT2000 diffractometer. The element composition was analyzed by scanning electron microscopy coupled with energy
dispersive X-ray spectroscopy (SEM-EDX). Magnetization measurements were performed by means of Quantum Design magnetic property measurement system (MPMS). The electrical resistivity was measured via a standard four-probe technique in Quantum Design physical property measurement system (PPMS).

3. Result and discussion

Figure 1 shows a powder X-ray pattern for the present polycrystalline sample. All peaks can be assigned by the cubic pyrochlore structure, which confirms single phase. The lattice constant is estimated to be 10.406(5) Å, larger than 10.3940(4) Å for a high-purity single crystal [5, 9]. From the relation of the ionic radius, \( R(\text{Pr}) > R(\text{Ir}) \), the enlargement is attributed to that excess Pr ions are introduced into the Ir sites, namely, “Pr-stuffing”. This can be reasonably explained by the loss of iridium oxide due to the evaporation during the solid state synthesis of the present sample. Our SEM-EDX analysis suggests Pr stuffing level to be around several %. However, we note that it is difficult to determine the level by our SEM-EDX analysis due to the accuracy of this method (error bar in Pr/Ir being several %). A high-resolution method, such as neutron diffraction and synchrotron x-ray diffraction, is highly required to complete structural analysis.

![Figure 1: A powder x-ray diffraction pattern for the present polycrystalline sample of \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) taken at room temperature. All peaks are indexed as the cubic pyrochlore structure. The indexes for tiny peaks are not shown. The weak, broad structure seen in the 2\( \theta \) range around 20-30 degrees originates from a glass plate sample holder.](image)

As in the case for high-purity single crystals [5], at a high temperature region (> 100 K), the temperature dependence of the magnetic susceptibility follows Curie-Weiss law with a constant term \( \chi_0 \chi = \chi_0 + \chi/(T - \theta_{\text{CW}}) \) (not shown). The fit yields \( \chi_0 = 3 \times 10^{-3} \) emu/mol-Pr, effective moment \( p_{\text{eff}} = 2.8 \mu_B \), and Weiss temperature \( \theta_{\text{CW}} = -6 \) K (antiferromagnetic). |\( \theta_{\text{CW}} \)| is smaller than that for single crystals (|\( \theta_{\text{CW}} \)| = 20 K).

Now we turn to the electrical transport properties. Figure 2 exhibits the temperature dependence of the electrical resistivity \( \rho(T) \) down to 0.4 K in 0 Oe. Due to the grain boundary scattering, \( \rho(T) \) in the present polycrystalline sample is about one order of magnitude larger than that in a single crystalline sample [5]. As shown in the main panel, \( \rho(T) \) gradually decreases as \( T \) decreases at a high temperature
This confirms the metallic property of the present sample. In addition, \( \rho(T) \) shows a minimum at around 20 K (inset), similarly to the case for single crystals [5]. What is remarkable here is a clear drop in \( \rho(T) \) at \( T \approx 0.8 \) K (inset). No corresponding anomaly was reported in previous studies in this temperature range. The most reasonable explanation for this phenomenon is the onset of phase transition into some sort of ordered state which reduces the spin scattering. Note that the phase transition is confirmed by our specific heat and magnetic susceptibility measurements, which will be published elsewhere [10].

![Figure 2: Temperature dependence of the electrical resistivity, \( \rho(T) \), for the present polycrystalline sample of \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) at 0 Oe below 300 K (main panel) and below 50 K (inset).](image)

We now discuss the possible origin of the difference in magnetism between present and previous samples. The Pr-stuffing, as observed in the present sample, is a most likely candidate. This modifies magnetic interactions and introduces randomness, which obviously affect the magnetism and may lead to emergence of the long-range order from the chiral spin liquid phase. In addition, oxygen deficiency is likely present in the sample, as indicated by the chemical formula of the Pr-stuffing system, \( \text{Pr}_{3+x}\text{Ir}_{2-x}\text{O}_{7.5} \) \( (x > 0) \), with the assumption of the valence of Ir to be 4+. Oxygen deficiency affects the anisotropy of \( \text{Pr}^{3+} \) magnetic moments by changing the crystalline electric field around \( \text{Pr}^{3+} \). This can also alter the carrier concentration and as a result the Kondo effects and RKKY interaction. Furthermore, a recent theory for Pr-based pyrochlores has revealed the significant importance of \( \text{Pr}^{3+}-\text{Pr}^{3+} \) superexchange coupling mediated by an intervening \( \text{O}^{2-} \) ion, which may be directly affected by oxygen deficiency [11, 12]. Another candidate is a difference in the structural parameters among samples, that is, lattice constant and oxygen position at 48f site being only structural parameters in pyrochlore compound. Indeed, this has been discussed to be responsible for the mysterious observation in the insulating Tb-based pyrochlores: \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) shows spin liquid state [13] while \( \text{Tb}_2\text{Sn}_2\text{O}_7 \) shows an ordered state [14], despite the fact that only main differences between them are the lattice constant and oxygen position. It cannot be ruled out that this is also the case for the \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) system. At present, we cannot identify the origin for the phase transition in the present sample. Systematic studies to check the above possibilities are on progress.
It is not clear whether the possible phase transition is accompanied by a conventional magnetic dipole order. The above-mentioned recent theory has proposed that, based on an effective quantum pseudospin-1/2 model for Pr-based pyrochlores, spin quadrupolar order formed by four spins on a tetrahedron can be stabilized by the Pr$^{3+}$-Pr$^{3+}$ superexchange interaction \[11, 12\]. Further investigations on the ordered state by means of neutron and $\mu$SR experiments are highly required to explore such possibility. In addition, the understanding of how the ordered phase is connected to the chiral spin liquid is an interesting future subject.

4. Conclusion

We have investigated the structural, magnetic, and electrical transport properties of a newly synthesized polycrystalline sample of the metallic pyrochlore $\text{Pr}_2\text{Ir}_2\text{O}_7$. The powder x-ray diffraction measurement indicates the presence of the Pr-stuffing. The temperature dependence of resistivity for the present sample shows a clear drop at around 0.8 K, strongly suggesting that the emergence of a phase transition into some sort of ordered state, in contrast to the previously reported spin liquid behavior. Although the origin of the phase transition is not clear at present, our results spark further interests in $\text{Pr}_2\text{Ir}_2\text{O}_7$.

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