Low temperature magnetism of the metallic pyrochlore oxide
\( \text{Pr}_{2+x}\text{Ir}_{2-x}\text{O}_{7+\delta} \)

Kenta Kimura, Yasuo Ohta, and Satoru Nakatsuji

Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba, 277-8581, Japan

k_kimura@issp.u-tokyo.ac.jp and y-ohta@issp.u-tokyo.ac.jp

Abstract. \( \text{Pr}_{2}\text{Ir}_{2}\text{O}_{7} \) is a metallic pyrochlore compound which has been revealed to form a spin liquid phase by recent studies. Here we report results of magnetic and electrical transport properties of a newly synthesized polycrystalline sample of \( \text{Pr}_{2+x}\text{Ir}_{2-x}\text{O}_{7+\delta} \) with excess Pr. A clear anomaly in the temperature dependence of the electrical resistivity is observed at 0.8 K, suggesting a phase transition into some sort of ordered state.

1. Introduction

It has been widely recognized that geometrical frustration due to certain lattice symmetries based on triangle motifs can be a source stabilizing novel states of matter [1, 2]. Particularly, physics of spins residing on a three dimensional pyrochlore lattice consisting of a corner sharing network of tetrahedra has been extensively studied experimentally and theoretically [3, 4]. A well-known example is a pyrochlore compound with the general formula \( A_2B_2O_7 \) (\( Fd-3m \) space group), in which both \( A \) and \( B \) sites individually form a pyrochlore lattice [5]. A wide variety of exotic states have been discovered in insulating pyrochlore compounds, such as spin ice in \( \text{Ho}_2\text{Ti}_2\text{O}_7 \) [6] and \( \text{Dy}_2\text{Ti}_2\text{O}_7 \) [7] and spin liquid in \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) [8].

Much attention has been currently devoted to pyrochlore \( \text{Pr}_2\text{Ir}_2\text{O}_7 \), a rare example of a metallic frustrated spin system [9-12]. 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 investigate the correlation between frustrated magnetism and mobile electrons. Indeed, a single crystal study revealed that despite relatively high Weiss temperature of \( \approx 20 \text{ K} \), the system exhibits no long-range order and instead forms spin liquid phase at least down to \( T_f = 110 \text{ mK} \), where a partial spin freezing was found. Besides, the Kondo effect is observed, indicating that the frustrated magnetism correlates with conduction electrons through the Kondo coupling [10]. Furthermore, a spontaneous Hall effect in the absence of uniform magnetization has been discovered in the spin-liquid phase [12]. This observation suggests that \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) is the first example of a chiral spin liquid where time reversal symmetry is macroscopically broken without magnetic dipole order.

In frustrated spin systems, an external perturbation such as magnetic field and chemical disorder often destabilizes a spin liquid state, and, as a result, a novel ordered phase might emerge. Here, we have investigated magnetic and electrical transport properties of a newly synthesized polycrystalline sample of \( \text{Pr}_{2+x}\text{Ir}_{2-x}\text{O}_{7+\delta} \) with an off-stoichiometric composition, \( x = 0.4(3) \), and found a possible phase transition into some sort of ordered phase. An origin of the phase transition will be discussed.
2. Experimental
The polycrystalline sample of $\text{Pr}_2+x\text{Ir}_2-x\text{O}_{7+\delta}$ was prepared according to Ref. [13]. The appropriate amounts of Pr$_6$O$_{11}$ (99.9%), and IrO$_2$ (> 99.9%) were well mixed together and pressed into a pellet. The pellet was wrapped with a Pt-foil, placed in a silica tube, sealed under vacuum, and then fired at 1423 K for about 5 days with several intermediate gridings. Powder x-ray diffraction confirmed the single pyrochlore phase ($Fd-3m$) of the sample. Scanning electron microscopy coupled with energy dispersive x-ray was used to analyse the composition and yields $x = 0.4(3)$, off-stoichiometry with excess Pr [14]. Magnetization measurements were performed using Quantum Design magnetic property measurement system (MPMS). The electrical resistivity was measured by means of a standard four-probe technique in Quantum Design physical property measurement system (PPMS).

3. Results and discussion
We show in Figure 1 the magnetic susceptibility $\chi = M/H$ as a function of temperature (2-300 K). No magnetic phase transition is observed in this temperature range. As seen in the inverse susceptibility $(1/\chi)$, the data above 100 K can be well fitted by the Curie-Weiss law with an additive constant term, $\chi = \chi_0 + C/(T - \theta_{CW})$, and the fit yields $\chi_0 = 1.3 \times 10^{-3}$ emu/mol-Pr, effective moment $p_{eff} = 3.0 \mu_B$, and Weiss temperature $\theta_{CW} = -13$ K (antiferromagnetic). These values are consistent with the previous studies based on polycrystalline samples [9] and stoichiometric single crystals of Pr$_2$Ir$_2$O$_7$ [10]. Note that, in the previous polycrystalline study [9], no information on the chemical composition (i.e. Pr/Ir ratio) of the sample was reported.

Figure 2 provides the temperature dependence of the electrical resistivity $\rho(T)$ down to 0.4 K at 0 T. At a high temperature region, $\rho(T)$ gradually decreases as $T$ decreases, confirming the metallic property of the present sample. In addition, $\rho(T)$ shows a minimum at around 20 K, similarly to the case for single crystals. What is remarkable here is a clear drop in $\rho(T)$ at $T \approx 0.8$ K. 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. The phase transition is confirmed by our specific heat and magnetic susceptibility measurements, which will be published elsewhere [15].
We now discuss the possible origin of the difference in magnetism between present and previous samples. A likely candidate is the sample off-stoichiometry. There are two types of off-stoichiometry: the deviation of the ratio Pr/Ir from 1 and oxygen deficiency. The former modifies magnetic interactions and introduces randomness, which obviously affects the magnetism. The latter is also important because this should affect anisotropy of Pr\(^{3+}\) magnetic moments through the variation of crystalline electric field made by O\(^{-2}\) ions around Pr\(^{3+}\). Furthermore, a recent theory for Pr-based pyrochlores has revealed the significant importance of Pr\(^{3+}\)-Pr\(^{3+}\) superexchange coupling mediated by an intervening O\(^{-2}\) ion, being also affected by the oxygen deficiency [16]. Finally, it can also alter the carrier concentration and as a result the Kondo effects and RKKY interaction. Another possibility is the difference in structural parameters among samples, that is, lattice constant and oxygen position at 48f site being only structural parameters in pyrochlore compounds. Indeed, this may be responsible for the mysterious observation in the insulating Tb-based pyrochlores: Tb\(_2\)Ti\(_2\)O\(_7\) shows spin liquid state [8] while Tb\(_2\)Sn\(_2\)O\(_7\) shows an ordered state [17], despite the fact that only main differences between them are lattice constant and oxygen position. It cannot be ruled out that this is also the case for the Pr\(_2\)Ir\(_2\)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 [16]. Further investigations on the ordered state by means of neutron and \(\mu\)SR experiments are highly required to explore such possibility. Furthermore, 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 temperature dependence of the magnetic susceptibility and electrical resistivity of a newly synthesized polycrystalline sample of the metallic pyrochlore Pr\(_{2+x}\)Ir\(_{2-x}\)O\(_{7+\delta}\) with excess Pr. Although the magnetic susceptibility of the present sample is similar to the results of previous studies, a clear drop in resistivity is found at 0.8 K, which has been never observed. This strongly suggests that the system experiences a phase transition into some sort of ordered state, in
sharp 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 Pr$_2$Ir$_2$O$_7$.

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