Metallic Spin-Liquid Behavior of the Geometrically Frustrated Kondo Lattice $Pr_2Ir_2O_7$

S. Nakatsuji,[1] Y. Machida,[1] Y. Maeno,[1,2] T. Tayama,[3] T. Sakakibara,[3] J. van Duijn,[4] L. Balicas,[5] J. N. Millican,[6]
R. T. Macaluso,[6] and Julia Y. Chan[6]
[1]*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*
[2]*International Innovation Center, Kyoto University, Kyoto 606-8501, Japan*
[3]*Institute for Solid State Physics (ISSP), University of Tokyo, Kashiwa 277-8581, Japan*
[4]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, United Kingdom*
[5]*National High Magnetic Field Laboratory (NHMFL), Tallahassee, Florida 32310, USA*
[6]*Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA*
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Strongly frustrated magnetism of the metallic pyrochlore oxide $Pr_2Ir_2O_7$ has been revealed by single crystal study. While Pr $4f$ moments have an antiferromagnetic RKKY interaction energy scale of $|T^*| = 20$ K mediated by Ir $5d$-conduction electrons, no magnetic long-range order is found except for partial spin freezing at 120 mK. Instead, the Kondo effect, including a $\ln T$ dependence in the resistivity, emerges and leads to a partial screening of the moments below $|T^*|$. Our results indicate that the underscreened moments show spin-liquid behavior below a renormalized correlation scale of 1.7 K.

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Geometrically frustrated magnets have attracted great interest because of the possible emergence of novel magnetic phases at low temperatures resulting from the suppression of conventional order. Among them, the three-dimensional pyrochlore lattice of corner sharing tetrahedra has been studied extensively [1]. It is predicted theoretically that Heisenberg spins on a pyrochlore lattice with nearest-neighbor antiferromagnetic (AF) coupling form a spin-liquid state at $T = 0$ K [2]. However, only a few compounds are believed to display a spin-liquid phase, such as the insulator $Tb_2Ti_2O_7$ [3].

In metallic systems, the frustration inherent to the pyrochlore lattice might also lead to new types of electronic behavior. One remarkable possibility is the predominance of the Kondo effect, and concomitant heavy-fermion behavior, in nearly localized d- and f-electron systems where the Kondo temperature is generally too small to overcome magnetic order without the frustration. Prominent examples are the heavy-fermion behavior in LiV_2O_4 and $Y(Sc)Mn_2$ with itinerant d-electron spins on a pyrochlore lattice [4,5].

Connecting the two exotic states of frustrated magnets, insulating spin-liquid and itinerant heavy fermions, there is another exciting yet unprecedented possibility of *metallic spin liquid* [6,7]. Ground states in f-electron based Kondo lattices are generally classified into Fermi liquid and magnetic regimes as the result of the competition between the Kondo effect and RKKY interactions. If the lattice has geometrical frustration and the transition temperature is depressed, the underscreened moments may stay disordered even in the magnetic regime, and form a metallic spin liquid on the *geometrically frustrated Kondo lattice*. (See the inset of Fig. 1.)

There has been a number of reports on *metallic* systems among the $A_2B_2O_7$ pyrochlore oxides possessing localized moments [1]. Yet, none is known to remain magnetically disordered down to the lowest temperatures except for the newly developed pyrochlore iridates [8]. In particular, the AF correlated Pr $4f$ moments of $Pr_2Ir_2O_7$ remain paramagnetic down to at least 0.3 K in the metallic state due to the Ir $5d$-conduction bands [8]. This places $Pr_2Ir_2O_7$ as a candidate for a geometrically frustrated Kondo lattice.

Here we report on strongly frustrated magnetism in single crystals of $Pr_2Ir_2O_7$. We find that the $\langle 111 \rangle$ Ising-like Pr^{3+} moments have an AF RKKY interaction energy scale $|T^*| = 20$ K. However, the dc magnetization down to 70 mK does not exhibit any trace of long-range order (LRO), except for an indication of partial freezing at 120 mK. Instead, the Kondo effect emerges below $|T^*|$ and leads to a partial screening of the $4f$ moments, re-

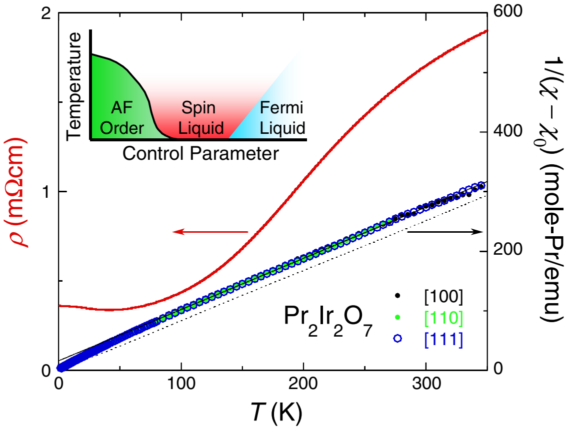

FIG. 1 (color online). Zero-field resistivity $\rho(T)$ (left axis), and the inverse of susceptibility $(\chi - \chi_0)^{-1}(T)$ (right axis) measured under a field of 100 mT along [100], [110], and [111]. The solid line represents a fit to the Curie-Weiss law, while the broken line indicates $(\chi_{CEF} - \chi_{vv})^{-1}$ based on the crystal electric field analysis. Inset: the schematic phase diagram for geometrically frustrated Kondo lattices.

normalizing the AF interaction to $|\theta_W| = 1.7$ K. Below $|\theta_W|$, the underscreened moments show spin-liquid behavior as indicated by the $\ln T$ dependence of the susceptibility and the $T^{1/2}$ dependence of the specific heat, as predicted for a frustrated Kondo lattice [6,7].

Single crystals of $Pr_2Ir_2O_7$ of 1 mm^3 in size were grown using a flux method for the first time at Kyoto [9]. A standard four-probe method was employed for resistivity measurements. Magnetotransport measurements were performed at the NHMFL dc field facility using a sample rotator. Specific heat C_P was measured by the thermal relaxation method down to 0.35 K. Magnetization measurements between 1.8 and 350 K were performed using a commercial SQUID magnetometer. Magnetization between 0.07 and 2.5 K and at fields up to 13 T was measured by the Faraday balance method using a dilution refrigerator at ISSP [10]. Single crystal four-axis x-ray diffraction analysis performed at LSU confirmed a well-ordered pyrochlore structure with Fd-3m symmetry with $a =$ 10.3940(4) Å (300 K) and 10.3850(4) Å (105 K) [9]. Energy dispersive x-ray analysis measurements found no trace of impurities.

The metallic transport of $Pr_2Ir_2O_7$ is shown in Fig. 1. No anisotropy was found with respect to the current direction. The resistivity $\rho(T)$ steeply decreases on cooling and saturates at a large residual resistivity $\rho_0 \sim$ 360 $\mu\Omega$ cm. On the other hand, a carrier density of 2.6×10^{20} cm^{-3} (1.8%/Pr), estimated from our preliminary Hall effect measurements at low T, yields a mobility of $\sim$70 cm^2/V sec for a single carrier model. This confirms the high quality of our single crystals, and shows that the low carrier density is the origin of the large ρ_0.

The crystal electric field (CEF) scheme of Pr^{3+} has been determined by inelastic neutron scattering measurements at 5 K [11]. Our analysis reveals the following two points: (i) nine multiplet levels of Pr^{3+} split into a ground-state doublet, three excited-singlets (162, 1218, 1392 K) and two excited doublets (580, 1044 K); and (ii) the Γ_3 ground-state doublet is magnetic with local $\langle 111 \rangle$ Ising anisotropy whose strength is $\sim$160 K. Because of the large separation between CEF levels, the magnetism discussed below comes solely from the ground doublet.

The inverse susceptibility $(\chi - \chi_0)^{-1}(T)$ is shown in Fig. 1. No anisotropy is found under a field of 0.1 T applied along [100], [110], and [111]. $\chi_0 = 1.25 \times 10^{-3}$ emu/mole-Pr is determined by a Curie-Weiss (CW) analysis above 100 K using the formula $\chi = \chi_0 + C/(T - T^*)$. This agrees with the sum of the Van Vleck term ($\chi_{vv} = 7.0 \times 10^{-4}$ emu/mole-Pr), as estimated from the above CEF scheme, and a Pauli paramagnetic term ($\chi_p \sim 5.0 \times 10^{-4}$ emu/mole-Ir) from the Ir 5d-conduction electrons, as in the metallic phase of $(Y, Ca)_2Ir_2O_7$ [12]. The effective moment $g_J\sqrt{J_z(J_z+1)} = 3.06\mu_B$ for the ground doublet is lower than the Pr^{3+} multiplet value ($3.62\mu_B$) due to the CEF. The AF Weiss temperature $T^* = -20.0$ K is most likely due to the RKKY interactions of the 4f moments for the following three reasons. (i) CW analysis of the susceptibility $\chi_{CEF}(T)$ computed using the above CEF scheme indicates a negligibly small CEF contribution (+0.77 K) to T^* (Fig. 1). (ii) Single-ion Kondo coupling cannot be as large as 20 K. In fact, few Pr-based compounds show Kondo effect because of Hund coupling in the Pr^{3+} $4f^2$ configuration which strongly reduces the Kondo temperature T_K [13]. Moreover, the low carrier concentration should also considerably decrease T_K [14]. (iii) The 4f moment superexchange and dipolar interactions in insulating pyrochlore magnets are normally of the scale of $\sim$1 K. Actually, $T^* = +0.35$ K for $Pr_2Sn_2O_7$, an insulating analog of $Pr_2Ir_2O_7$ [15]. Thus, a several orders of magnitude stronger T^* indicates that it is due to the RKKY interaction.

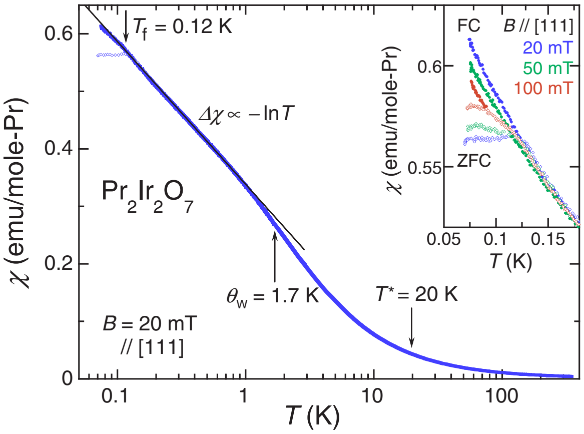

FIG. 2 (color online). dc susceptibility $\chi(T)$ as a function of $\ln T$ under a field of 20 mT along [111]. The $\ln T$ dependence is indicated by the solid line. Low T dependence under various fields is shown in the inset in a linear scale. Both field-cooled (FC) and zero-field-cooled (ZFC) data are shown.

Normally, one expects a Pr-based low carrier system like $Pr_2Ir_2O_7$ to be deep in a magnetic regime, and to exhibit magnetic LRO at the intersite interaction scale $|T^*|$, if the system has no magnetic frustration [16]. Remarkably, however, no anomalies due to a magnetic transition were detected in $\chi(T)$, except for freezing at $T_f = 120$ mK (Fig. 2). A large ratio $|T^*|/T_f = 170$ is a strong indication of frustrated magnetism in $Pr_2Ir_2O_7$. In addition, an anomalous $\ln T$ dependence of $\chi(T)$ was observed over a decade of T between T_f and 1.4 K. This diverging $\chi(T)$ as $T \rightarrow 0$ K, combined with an exact pyrochlore lattice symmetry, confirmed by single crystal x ray, excludes the possibility that the non-Kramers ground doublet is split into nonmagnetic singlets. Instead, this $\ln T$ dependence, distinct from the mean-field CW behavior, indicates that the 4f moments are strongly fluctuating even at $T \ll |T^*|$ owing to the magnetic frustration, forming a liquidlike short-range order. In addition, the zero-field-cooled (ZFC) $\chi(T)$ only levels off below T_f as set by a bifurcation of the field-cooled and ZFC curves (inset of Fig. 2). Normally for spin glasses, the ZFC curve is expected to show a steep decrease below T_f because most spins get

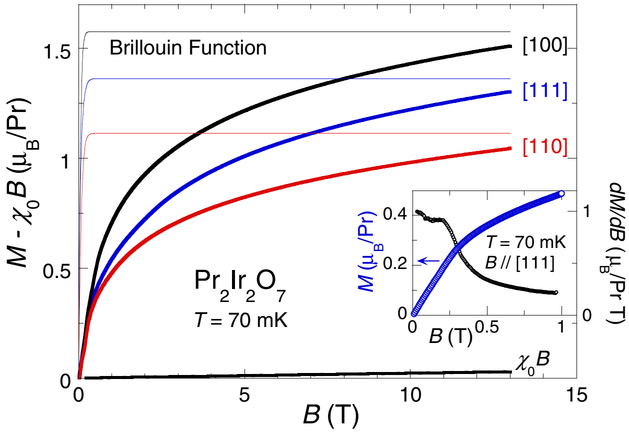

FIG. 3 (color online). Field dependence of the magnetization M (thick curves) and the Brillouin function of $\langle 111 \rangle$ Ising spins (thin curves) for fields along [100], [110], and [111]. Inset: low field M and its derivative dM/dB along [111].

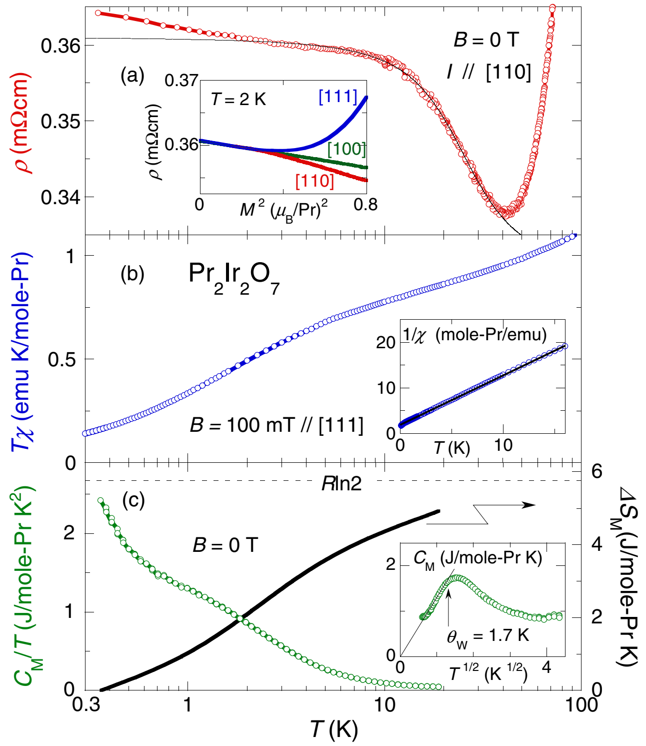

FIG. 4 (color online). (a) Low T resistivity $\rho(T)$ vs $\ln T$. Inset: transverse magnetoresistance vs the square of the magnetization M^2 along various axes. (b) Effective Curie constant $C(T) \equiv T\chi(T)$ vs $\ln T$. Inset: inverse susceptibility $\chi^{-1}(T)$. (c) Magnetic part of the specific heat divided by temperature C_M/T (left axis) and the entropy $\Delta S_M(T) \equiv S(T) - S(0.35\text{ K})$ (right axis) as a function of $\ln T$. The horizontal broken line indicates $\Delta S_M(T) = R\ln 2$. Inset: C_M as a function of $T^{1/2}$.

frozen at T_f. The observed T-independent behavior suggests that only a partial fraction of spins freezes, while the majority remain liquid.

The $\langle 111 \rangle$ Ising-like anisotropy of the $4f$ moments is confirmed by the field dependence of the magnetization $M(B)$ along [100], [110], and [111] at 70 mK (Fig. 3). The $4f$ ground-state-doublet contribution (thick curves) is estimated by subtracting the sum of the Van Vleck and Pauli paramagnetic contributions, which is estimated from $\chi_0 B$ (Fig. 3). At 13 T, M tends to saturate and approaches a Brillouin function (thin curves) for noninteracting, local $\langle 111 \rangle$ Ising spins with $g_J J_z = 2.69$, consistent with the CEF analysis [11]. This slow saturation at the field scale, $B^* \equiv k_B|T^*|/(g_J \mu_B J_z) \sim 11$ T, confirms an AF coupling with an energy scale of $|T^*| = 20$ K. At low fields, M becomes isotropic (Fig. 3), as expected for $\langle 111 \rangle$ Ising spins on a pyrochlore lattice [17]. Below 0.3 T, M changes displaying a nearly constant derivative dM/dB (inset of Fig. 3). This departure from a Brillouin function also suggests liquidlike short-range correlations.

When such $\langle 111 \rangle$ Ising spins on a pyrochlore lattice interact only through a nearest-neighbor AF coupling J, mean-field theory predicts an "all-in and all-out" type of LRO to appear at $T \sim J$ [18]. This indicates that in $Pr_2Ir_2O_7$, effects beyond the mean-field theory of nearest-neighbor AF interaction, such as quantum fluctuations and longer-range couplings, are crucial to suppress the LRO down to $T \ll |T^*|$. Observed indications of such effects are (1) the Kondo coupling between the $4f$ moments and the $5d$-conduction electrons, and (2) the RKKY long-range interactions between the $4f$ moments.

Although rare, the Kondo effect in Pr-based compounds [19,20] and low carrier systems [14] has been reported. The first evidence of Kondo effect in $Pr_2Ir_2O_7$ is the $\ln T$ dependence of the resistivity [Fig. 4(a)]. For such a dependence in a stoichiometric high-quality metal, two mechanisms can be considered: (i) CEF effect and (ii) Kondo effect. Since the gap to the first excited level is ~160 K, the $\ln T$ dependence below 50 K cannot be due to a CEF effect. Thus, the observed $\ln T$ dependence is likely due to the Kondo effect, and in fact, over a decade in T between 3 K and 35 K, $\rho(T)$ can be fit to the Hamann's expression (solid line) with $T_K = 25$ K [21]. Interestingly, T_K is close to $|T^*|$, and suggests that it is not the single-ion screening, but the intersite screening that leads to the Kondo effect, as discussed for low carrier-density and AF correlated Kondo lattices [14,22]. In addition, the field dependence of the resistivity is consistent with the Kondo effect [13]; the negative magnetoresistance is proportional to M^2 for all axes under fields up to $2\text{ T} < B^*$ [inset of Fig. 4(a)].

Second, the Kondo effect is also seen in the low T decrease of the effective Curie constant $C(T) \equiv T\chi(T)$; see Fig. 4(b). The rapid decrease in $C(T)$ below 10 K suggests that the moment size diminishes owing to Kondo screening. Correspondingly, $\chi^{-1}(T)$ follows the CW law over a decade in T from 1.5 to 16 K [solid line in the inset of Fig. 4(b)], yielding a slightly smaller effective moment $2.69\mu_B$, and a reduced Weiss temperature, $|\theta_W| = 1.7$ K, in comparison with the high T values ($3.06\mu_B$, 20 K). These results and the crossover to $\ln T$ dependence below $|\theta_W|$ indicate partial screening of $4f$ moments, which dramatically renormalizes the AF interaction energy scale and consequently leads to a correlated liquid of underscreened moments below $|\theta_W|$. The monotonic increase of $\rho(T)$ on cooling [Fig. 4(a)] indicates incoherent spin scattering in the spin-liquid state at $T < |\theta_W|$.

Further evidence for the Kondo effect and spin-liquid formation can be found in the T dependence of the magnetic part of the specific heat C_M. C_M is obtained by subtracting from C_P, (i) the lattice contribution estimated from $C_P(T)$ of the isostructural, $4f$ moment free $Eu_2Ir_2O_7$, and (ii) the $1/T^2$ Pr-nuclear quadrupole contribution estimated by a standard analysis of the field dependence. No evidence of LRO, but a rapid increase up to $\sim$2.5 J/mole- Pr K^2 is seen in C_M/T below $|T^*|$, attributable to the Kondo screening [Fig. 4(c)]. Correspondingly, the entropy $\Delta S_M(T) \equiv S(T) - S(0.35\text{ K})$ estimated by integrating C_M/T shows a gradual decrease from the $R\ln 2$ of the ground doublet below $|T^*| = 20$ K. Significantly, C_M forms a broad peak around $T \sim |\theta_W|$, and decreases on cooling with a $T^{1/2}$ dependence between 1.8 and 0.4 K [inset of Fig. 4(c)]. This peak indicates the formation of a correlated spin-liquid below $|\theta_W|$. S_M also follows the $T^{1/2}$ dependence at low Ts, indicating the presence of much more highly degenerate magnetic states than in a Fermi liquid with a T-linear entropy. This also represents additional evidence for magnetic frustration.

The experiments reported here reveal the following remarkable properties: (1) a large ratio $|T^*|/T_f = 170$, (2) Kondo effect below $|T^*|$, (3) $\ln T$ dependence of $\chi(T)$ below $|\theta_W|$, (4) peak formation of C_M at $T \sim |\theta_W|$ with a $T^{1/2}$ dependence below $|\theta_W|$, and (5) a linear increase of the low-T $M(H)$ below $B_c = 0.3$ T. Observations (1) and (2) indicate that $Pr_2Ir_2O_7$ is a strongly frustrated Kondo lattice, most likely ascribable to the geometrical frustration inherent to the pyrochlore structure. Moreover, observations (3)–(5) indicate spin-liquid behavior at $T \leq |\theta_W|$ and $B \leq B_c$. The boundaries $|\theta_W|$ and B_c have energy scales of the same order of magnitude, as evident from the relation $k_B|\theta_W|/(g_J\mu_B J_z) = 0.9$ T.

Notably, observations (3) and (4), especially the T dependence of χ and C_M, agree well with the spin-liquid behavior predicted by dynamical mean-field theory for a frustrated Kondo lattice [6,7]. Near a quantum critical point separating spin-liquid and Fermi liquid (see the inset of Fig. 1), the ground state is expected to be so sensitive to disorder that even undetectable defects may cause spin freezing [7]. The observed low T cutoff of the asymptotic forms of $\chi(T) \propto \ln T$ and $C_M \propto T^{1/2}$ may come from a tendency towards spin freezing of the decoupled spins caused by disorder [7]. To confirm this, μSR measurements are now in progress.

To summarize, our single crystal study has revealed that $Pr_2Ir_2O_7$ is a pyrochlore Kondo lattice with $\langle 111\rangle$ Ising-like $4f$ moments. The following four-stage process is observed: (1) $T > |T^*|$, Pr $4f$ moments are decoupled from Ir $5d$-conduction electrons; (2) $|T^*| > T > |\theta_W|$, the Kondo effect leads to the screening of the $4f$ moments; (3) $|\theta_W| > T > T_f$, underscreened moments form a spin liquid; and (4) $T_f > T$, the moments partially freeze. The magnetic LRO expected at the RKKY coupling scale is suppressed due to geometrical frustration, but instead the Kondo effect is stabilized to partially screen the $4f$ moments, and leads to the "metallic spin-liquid" behavior. Further investigation is necessary to clarify the origin of the geometrical frustration in the pyrochlore magnet.

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