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Magnetic Properties of $Pr_2Ir_2O_7$ Thin-film using X-Ray Magnetic Circular Dichroism

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INTRODUCTION: Rare-earth pyrochlore iridates ($RE_2Ir_2O_7$) consist of two interpenetrating cation sublattices, the *RE* with highly frustrated magnetic moments, and the iridium with extended conduction orbitals significantly mixed by spin-orbit interactions. The coexistence and coupling of these two sublattices create a landscape for discovery and manipulation of quantum phenomena such as the topological Hall effect, mass-less conduction bands and considered as a key ingredient for many exotic topological and quantum phases, whereas, thin films possess an extended control of the material system via symmetry-lowering effects such as *strain*. Rare-earth pyrochlore iridates ($RE_2Ir_2O_7$) have been the subject of much research interest as a result of predictions and observations such as bulk and edge massless conduction, frustrated magnetism, and metal-insulator transitions [1–3]. The f-d magnetic exchange interaction is considered to be the main feature in pyrochlore iridates. The key to the intriguing properties of $RE_2Ir_2O_7$ is the intimate coupling of two distinguishable sublattices of ionic *RE* and conducting *Ir* cations, as well as connecting oxygens. Each sublattice consists of alternating triangular and Kagome planes that are more easily visualized as forming a corner-sharing tetrahedral network. The *RE* magnetic-exchange interactions are mediated by the conducting Ir bands through the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [4]. As a result of the lattice geometry and antiferromagnetic nearest neighbour coupling, spins on the *RE* and *Ir* sublattices are constrained to point toward or away from the centre of one of the adjacent tetrahedral, forming frustrated spin-liquid correlations. The *RE* ions have typical local moments of a few Bohr magnetons and *Ir* adds the complexity due to its strong spin-orbit coupling, mixing together as the orbital and spin degrees of freedom.

$Pr_2Ir_2O_7$ is a unique member as it is a pyrochlore iridates which has magnetic and comparatively large A-site ion, Pr^{3+} ($4f^2$). this material has two active (Pr and Ir) sublattices metallic down to the lowest temperatures and shows a nonmagnetic character, even though an AFM-type RKKY interaction at 20 K between Pr-*4f* moments has been observed which is mediated through Ir-*5d* delocalized electrons [4,5]. As a result of various two-in–two-out magnetic configurations at the Pr sites with no net magnetic moment or long-range order. This material is metal and shows that AFM interaction is suppressed due to screening of *4f* moments through Kondo effect which decreases the Weiss temperature down to ~ 1.7K while $Pr_2Ir_2O_7$ shows a paramagnetic-metallic behaviour at room temperature [5].

Here we combine synchrotron-based x-ray spectroscopy techniques to provide direct evidence supporting the sublattice emergence of the Pr local moments in the epitaxial $Pr_2Ir_2O_7$ thin films. To get a better understanding of the electronic configuration of $Pr_2Ir_2O_7$, we compare the Pr M_5 and Pr M_4 x-ray magnetic circular dichroism (XMCD) results of our thin films.

1. EXPERIMENT: Polycrystalline samples of $PR_2Ir_2O_7$ have been prepared using standard solid-

state route synthesis. Powder ingredients of Pr_6O_{11} and IrO_2 (≥ 99.99% pure, M/s Sigma Aldrich) are mixed in stoichiometric ratio, grounded well and thereafter palletized and sintered in air at 1000-1160 ˚ C for 10 days with several grindings. YSZ (Yttria Stablized Zirconia) is widely used as an oxide crystal substrate for the epitaxial growth of thin-films which is generally used as one of the first materials applied to deposit high temperature superconducting thin-films. $Pr_2Ir_2O_7$ (100) single-

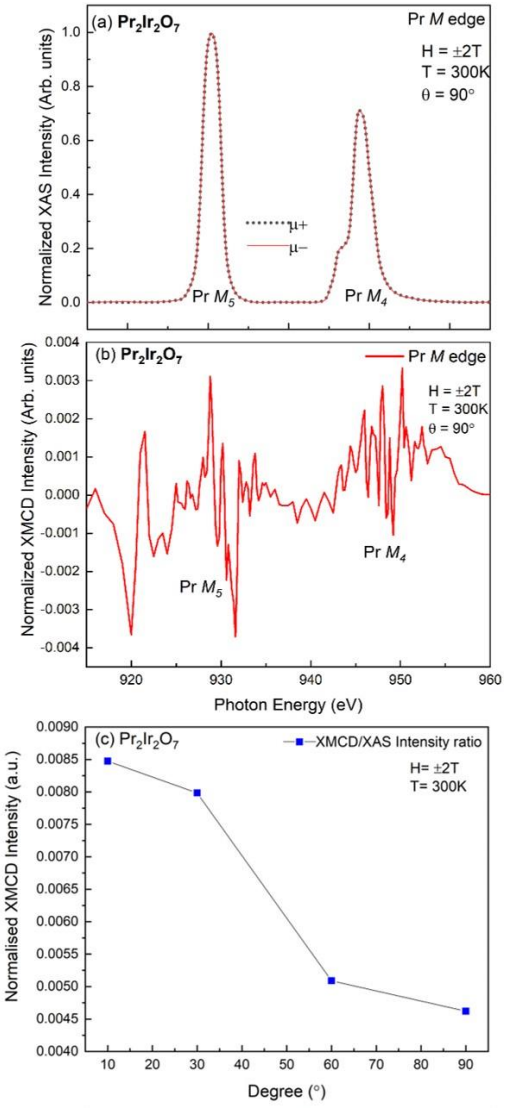

Fig. 1(a) Normalised XAS and (b) Normalised XMCD spectra of Pr $M_{4,5}$ edges of $Pr_2Ir_2O_7$ thin-films at magnetic-field ±2T, at variable angle 90° from sample-surface in 300K. Fig.1(c) represents XMCD/XAS Intensity ratio w.r.t. varying angle.

layer has been deposited on YSZ (001) substrate using Pulsed Laser Deposition (PLD) technique (KrF excimer laser, λ = 248 nm, repetition rate: 10 Hz, fluence: ~1.1 J cm^{-2} with pulse duration of 20 nsec.) at 500 °C under an oxygen atmosphere of 1.0 × 10^{-6} Torr. The single-layered epitaxial thin-film was then followed by inducing an in-situ annealing treatment for 2 hours in the temperature range of 550–590°C. X-ray spectroscopy, scattering, and imaging experiments were performed at the variable-polarization soft x-ray beam-line BL-16A of the Photon Factory (KEK, Japan). Experimental geometry of soft x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) experiments are shown in Fig. 1. The sample was placed in the vacuum chamber with a pressure of 10^{-9} Torr equipped with a 5 T superconducting magnet. XAS and XMCD signals were measured at ±0.1T, ±1T and ±2T varying magnetic-fields (only the data of ±2T has been produced here) with an energy resolution of 0.1 eV using the bulk-sensitive total fluorescence yield (TFY) method with a variable angle dependency of 10 ˚, 30 ˚, 60 ˚ and 90 ˚ from the sample–surface near Pr $M_{4,5}$ absorption edges with right and left circularly polarized (RCP and LCP) x-rays.

2. <u>RESULTS AND DISCUSSIONS:</u> We have also attempted to understand the conduction band state of Pr which is important for its role in governing the electronic and magnetic properties**.** The XAS spectra obtained with applied magnetic fields of +2.0 and -2.0 T are denoted by μ^+ and μ^- which represent left and right circularly polarized light, respectively as shown in Fig 1(*a*). The XMCD spectrum was recorded by taking a difference between the XAS spectra with negative and positive helicities of the circular polarized light as shown in Fig 1(*b*). It is known from literature that, $Pr_2Ir_2O_7$ is a paramagnetic metal at room temperature that turns into anti-ferromagnet at cryogenic temperatures below 1.7 K [3]. Due to the metallic nature of the $Pr_2Ir_2O_7$ thin-film, the Pr absorption peaks shows a singlet structure at the M_5 with energy E = 930.41 eV and at E = 948.78 eV M_4 edge is found to be arrived with a satellite feature at 946.48 eV. This signifies that the fine structures of Pr *3d* → *4f* transition should result from the localization of Pr *4f* electrons rather than the oxidation of the surface. This makes sense as the Pr 4*f* orbitals are fairly localized and overlap less with the distorted surrounding atoms. The position of M_5 and M_4 peaks is found to be around 930 and 949.3 eV, respectively which closely match with that for Pr^{3+} ions [2]. This suggests that Pr belongs in 3+ charge state. The observed fine structure of the XAS spectrum of Pr also corresponds to the ne calculated from the bulk sample [Fig. 1(a)] [2]. XMCD signal

measured in a magnetic field of B 2.0 T well above the saturation is shown in Fig.1(b) for Pr-edges. Despite that the magnitude of the XMCD measured at the $M_{4,5}$ edges of Pr, it is clear that the signs of the dichroic signals are almost same. The XMCD/XAS intensity ratio w.r.t. the angle variations (as shown in Fig 1(c)) from 10˚, 30˚, 60˚ and 90˚ predicts that the intensity ratio decreases with increasing angles normal towards the plane of the sample thin-film which signifies the existence of out-of-plane easy-axis in the sample. Such analysis from the XAS and XMCD data verifies that the $Pr_2Ir_2O_7$ is found to exhibit spin liquid behaviour where the system does not show any trace of magnetic ordering at room temperature. Instead, a partial spin freezing of Pr-*4f* moments is observed at 120 mK has been reported in literature.[4]

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