Experimental report

15/09/2023

Proposal: 5-26-223 **Council:** 10/2022

Title: Total scattering investigation on potential cation ordered Ir/Rh Ruddlesden-Popper phases

Research area: Chemistry

This proposal is a new proposal

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Samples: La2Sr2MgIrO8
La2Sr2MgRhO8

Instrument	Requested days	Allocated days	From	To
D1B	2	2	17/05/2023	19/05/2023
D4	2	0		

Abstract:

Materials with perovskite structure are one of the most interesting materials in the solid state physics and chemistry. Ruddlesden-Popper phases (RPs) can be considered as the bridge between perovskite phases and quasi two dimensional systems due to their layered structure. RPs have been the focus of intense research for spin-orbit coupling driven phenomena and the discovery of high Tc superconductivity in cuprate and ruthenate RPs. La2Sr2MgIrO8 and La2Sr2MgRhO8 are the first RPs iridates and rhodates with a possible cation order in the perovskite-like layers which is challenging to detect due to loss of translation symmetry of the cation ordering perpendicular to the perovskite like layers. Therefore only total neutron scattering using D1B and D4 will give us the information necessary to completely characterize magnetic and crystal structure.

Total scattering investigation on potential cation ordered Ir/Rh Ruddlesden-Popper phases

Experiment Report

Scientific background

Perovskites have long been a primary sandbox for the development of structure-property relationships and the research of physical phenomena in the solid state. A subset of these investigations concerns the Ruddlesden-Popper phases (RPs), which can be considered as perovskite-like with a reduced dimensionality aspect. While the number of noteworthy applications and studies in this domain are legion, the discovery of high Tc superconductivity in the cuprate RPs [1] marked a significant breakthrough as well as the unconventional superconductivity in ruthenate RPs [2]. More recently, iridate RPs have been the focus of intense research for spin-orbit coupling driven phenomena and possible proximity to superconductivity [3,4].

However, despite the considerable extent of work done in highly exciting RPs for physical phenomena, it is not widely known that much like the 3D perovskite, there is the possibility to impose cation order on the perovskite-like layers [5]. However, the detection of this cation ordering is challenging due to the possible loss of translational symmetry of the cation ordering perpendicular to the perovskite like layers, necessitating advanced structural characterization techniques. Here, we have prepared two novel RPs, one with $4d^5$ Rh^{4+} magnetic cations and one with $5d^5$ Ir^{4+} magnetic cations. To the best of our knowledge, these are the first possible cation ordered rhodate and iridate RPs, and we propose to study their local structure via total neutron scattering on D4 at the ILL.

Results of preliminary work

3 g of $La_2Sr_2MgIrO_8$ and 1.5 g $La_2Sr_2MgRhO_8$ were obtained using solid-state synthesis technique. $La_2Sr_2MgRhO_8$ powders were synthesized with minor nonmagnetic La_2O_3 impurities. In the $La_2Sr_2MgIrO_8$ sample minor La_2O_3 and Ir impurities were present. Preliminary refined X-ray powder diffraction patterns, fit to the single RP structure, are shown in Fig. 1 and 2. SQUID magnetic susceptibility versus temperature data for $La_2Sr_2MgRhO_8$ demonstrates paramagnetic behaviour down to 1.8K (Fig.5). Curie Weiss analysis of $La_2Sr_2MgRhO_8$ results in a Weiss temperature of –186 K and an effective moment of 1.66 μB per Rh. $La_2Sr_2MgIrO_8$ compound shows paramagnetic behaviour and a quite broad antiferromagnetic transition at ~ 40 K (Fig.6). Curie Weiss analysis of $La_2Sr_2MgIrO_8$ results in a Weiss temperature of -71 K and an effective moment of 1.38 μB per Ir. Both of these effective moment values compare to a theoretical 1.71 μB, demonstrating the increase in SOC upon moving from the rhodate sample to the iridate.

Previously, we have submitted this proposal and were granted the opportunity to perform NPD on these materials at the D1B beamline (Fig. 3,4). Here, we measured with two wavelengths to cryogenic temperatures, finding no long range magnetic order or deviation from the single Ruddlesden-Popper <u>average structure</u> (Fig. 7,8). The neutron diffraction data have a clear sample-oriented background shape which is not temperature dependent – likely diffuse scattering from disorder in the structure (from paracrystalline stacking faults, Sr/La disorder, and/or Mg/B' disorder along with associated local distortion fields). Since then, we have additionally collected synchrotron data from PETRA III to produce X-ray pair distribution functions (XPDFs). However, it is clear to us that the XPDFs lack key information about the local structure of the oxygen polyhedral around each metal, but rather primarily contains information about the metal-metal pairs throughout the structure. Additionally, we have performed electron diffraction experiments faintly indicating the local formation of superstructure peaks. Hence, we have decided, that it is worthwhile to return to ILL to remeasure these samples (already at ILL) on the D4 beamline to produce neutron pair distribution functions (NPDFs) to finalize our total picture of the structural features of these compounds.

[1] R. J. Cava et al, *Phys. Rev. Lett.* **58**, 408 (1987).
[2] Y. Maeno et al, *Nature* **372**, 532-534 (1994).
[3] B. J. Kim et al, *Science* **323**, 1329-1332 (2009).
[4] J. Kim et al, *Phys. Rev. Lett.* **108**, 177003 (2012).
[5] J. C. Burley et al, *J. Amer. Chem. Soc.* **124**, 620-628 (2002).
[6] M. L. Robinson et al, *Inorg. Chem.* **59**, 5, 3026–3033 (2020).

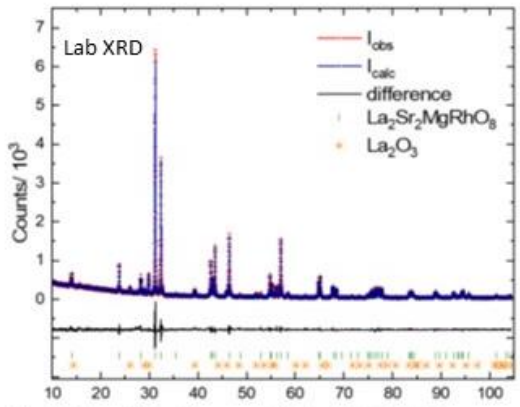

Fig.1 Rietveld refinement for $La_2Sr_2MgRhO_6$

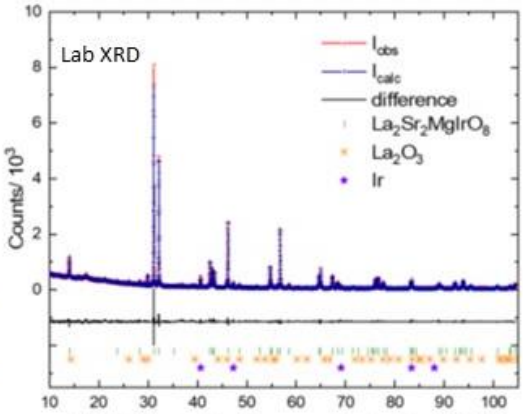

Fig.2 Rietveld refinement for $La_2Sr_2MgIrO_6$

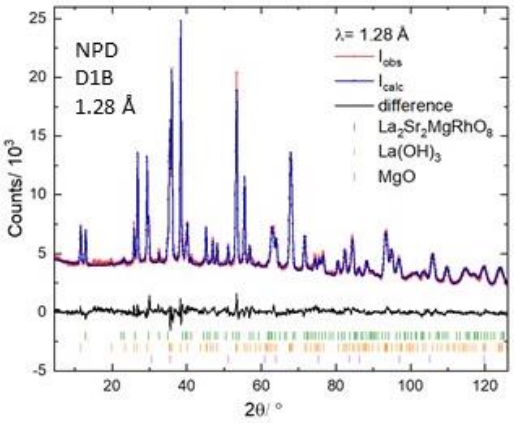

Fig. 3 Refined NPD data for $La_2Sr_2MgRhO_8$

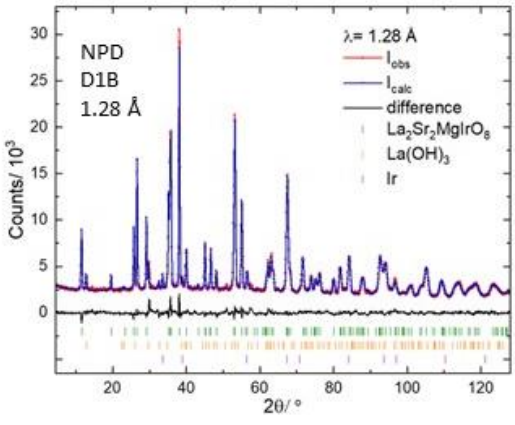

Fig. 4 Refined NPD data for $La_2Sr_2MgIrO_5$

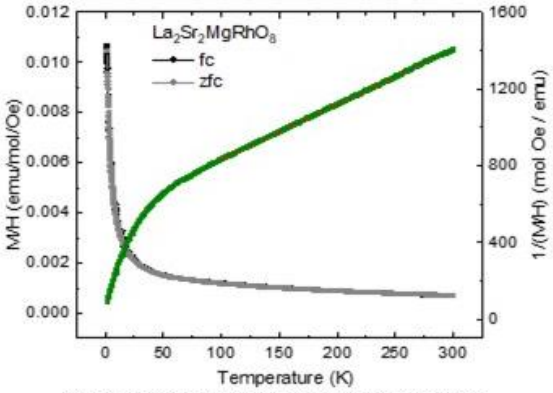

Fig.5 Temperature dependent magnetization for $La_2Sr_2MgRhO_8$

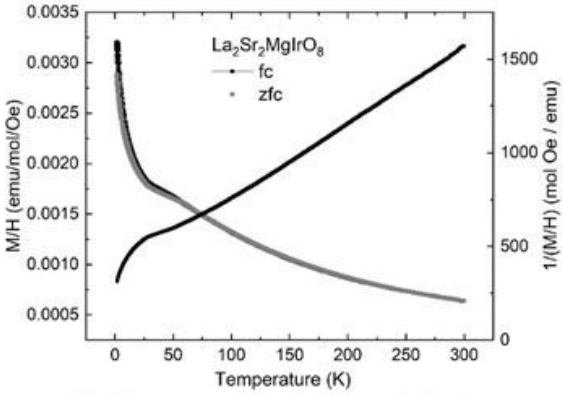

Fig.6 Temperature dependent magnetization for $La_2Sr_2MgIrO_8$

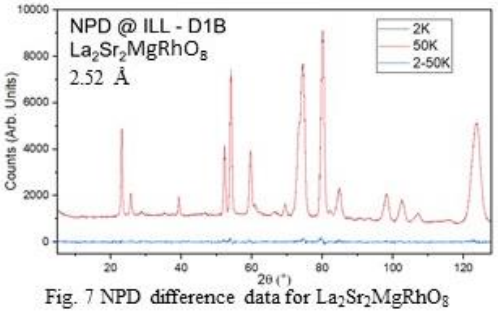

Fig. 7 NPD difference data for $La_2Sr_2MgRhO_8$

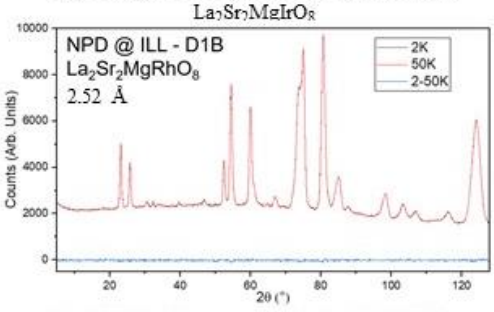

Fig. 8 NPD difference data for $La_2Sr_2MgRhO_8$