Experimental report

18/09/2024

Proposal:	**5-31-2966**	**Council:**	4/2023
Title:	Magnetic structures of strongly spin-orbit coupled iridates SrLa10Ir4O24 and Sr3La8Ir4O24		
Research area:	Physics		

This proposal is a resubmission of 5-31-2932

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Samples: SrLa10Ir4O24 and Sr3La8Ir4O24

Instrument	Requested days	Allocated days	From	To
D2B	1	1	29/09/2023	30/09/2023
D20	2	2	11/09/2023	13/09/2023

Abstract:

SrxLa11-xIr4O24 (1¿ x ¿ 5) is a fascinating family of iridates, where crossover from Ir4+ to Ir5+ within isolated IrO6 octahedra allows investigating the strongly spin-orbit-entangled quantum magnetic ground states. The susceptibility reveals an antiferromagnetic-like transition at around 10 K for the x ¿ 3.5 samples, and absence of anomaly in case of x¿4.0 samples. Furthermore, there is nonmonotonic variation of Curie-Weiss temperature in transiting from Ir4+ to Ir5+ with Sr-doping, indicative of subtle balance between coexisting ferro- and antiferromagnetic exchanges. However, detection of their true magnetic ground states and magnetic structures are not reported. We, therefore, propose neutron diffraction study of SrLa10Ir4O24 and Sr3La8Ir4O24 using D20 diffractometer. We have prepared 4g of each these samples and characterized using XRD, magnetic susceptibility and heat capacity measurements.

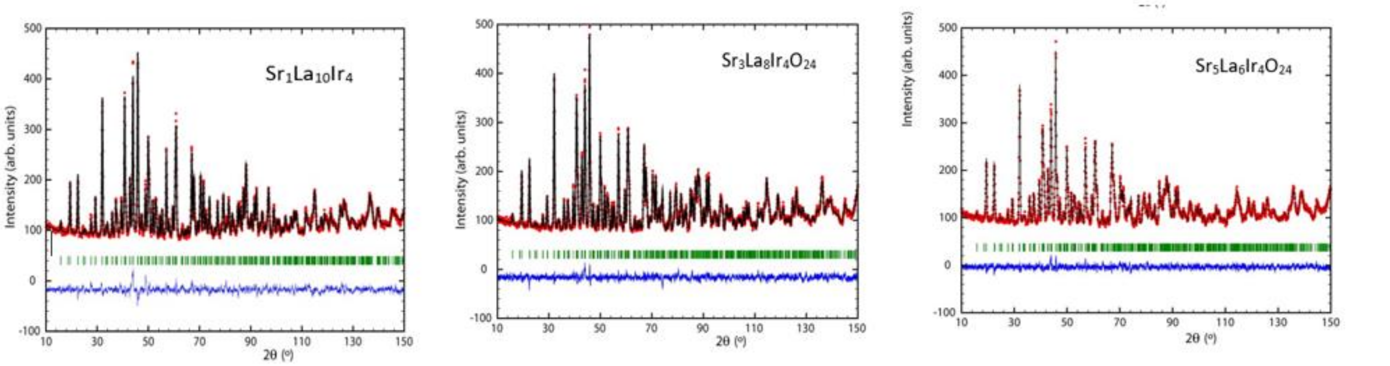


Fig.1 Room temperature neutron powder diffraction (NPD) patterns collected from the $Sr_xLa_{11-x}Ir_4O_{24}$ (x = 1, 3, 5) samples at D2B spectrometer of ILL, and subsequent structural refinements:

Each of these three samples has been satisfactorily refined using a pure single phase with tetragonal $I4_1/a$ space group and the refined structural parameters, such as lattice constants and atomic coordinates, turn out to be very similar with the previous report by Phelan et al. [Phys. Rev. B **91**, 155117 (2015)].
We then measured the NPD on x = 1 & 3 samples at 15 K at the D2B instrument of ILL with λ = 1.594 Å. The collected experimental NPD data along with the Rietveld refinement results for both the samples are presented below Clearly, there is no noticeable structural changes in either of the samples even at 15 K compared to the 300 K structural refinements.

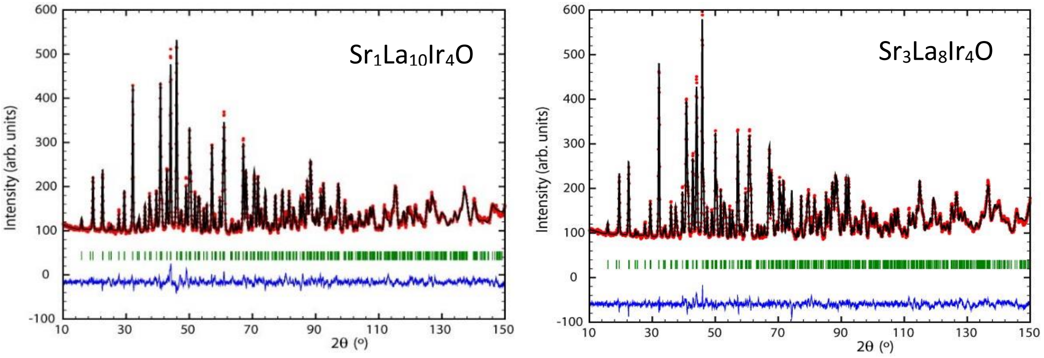


Fig.2 NPD data of x = 1 & 3 samples at 15 K at the D2B instrument.

Following this, the NPD data were collected on the D20 spectrometer of ILL with 42° Take-off angle and 2.415 Å neutron wavelength from the x = 1 & 3 samples at 15 K as well as 1.7 K to investigate the magnetic ordering and the ground state Ir spin structure.

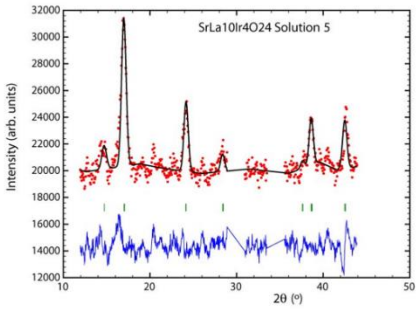
<u>$Sr_1La_{10}Ir_4O_{24}$ magnetic structure analysis:</u>
The (1.7 K – 15 K) data of $Sr_1La_{10}Ir_4O_{24}$ is plotted below..All the magnetic Bragg peaks can be indexed with the propagation vector k = 0 and the magnetic symmetry analysis was done using the MAXMAGN program of the Bilbao crystallographic server.
Among the following three allowed solutions,

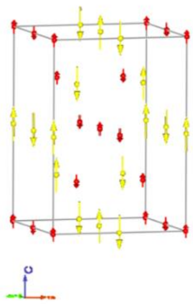
2 x 4 sites created for	Solution 3				Solution 4				Solution 5			4 x 2 sites created for
Ir_1 (0,0,0) and Ir_2 (0,0,½)	BV1	BV2	BV3		BV1	BV2	BV3		BV1	BV2	BV3	Ir_{11} (0,0,0), Ir_{12} (¾,¼,¼) and Ir_{21} (0,0,½), Ir_{22} (¾,¼,¾)
1: x,y,z	100	010	001		100	010	001		100	010	001	x,y,z
2: -x+½,-y,z+½	-100	0-10	001		-100	0-10	001		100	010	00-1	-x+½,-y,z+½
3: y+¾,x+¼,z+¼	010	-100	00-1		0-10	100	001					
4: y+¾,-x+¾,z+¾	0-10	100	00-1		010	-100	001					

Solution 4 can be rejected while the other two solutions, Solution 3 and Solution 5, lead to the refinements with nearly equal in goodness. It is important to note that in Solution 3 each of the two fourfold Ir-sites (Ir1 on 0,0,0 and Ir2 on 0,0,½) is linked according to the above table. In solution 5 each of the two fourfold sites is further divided into two independent twofold sites (Ir_{11} on 0,0,0 and Ir_{12} on ¾,¼,¼, Ir_{21} on 0,0,½ and Ir_{22} on ¾,¼,¾). Furthermore, it is worth mentioning that both solutions (solution 3 and solution 5) do not produce any magnetic diffraction intensity at the position of the excluded regions at 30° and 35°.
Solution 5: $P_{Mag} = 13.8$, $\chi^2 = 19.0$, $\mu_{Ir11} = \mu_{I\rho 12} = 0.24(1)\ \mu_B$, $\mu_{Ir21} = \mu_{Ir22} = 0.59(1)\ \mu_B$ or vice versa.

Magnetic moments along *c*. It is impossible to decouple Ir_{11} from Ir_{12} or Ir_{21} from Ir_{22}. Only BV3 is used, giving BV1 and/or BV2 additionally free leads to divergence.

Fig.3 The fit to the data and the magnetic structure of $Sr_1La_{10}Ir_4O_{24}$ at 1.7 K.





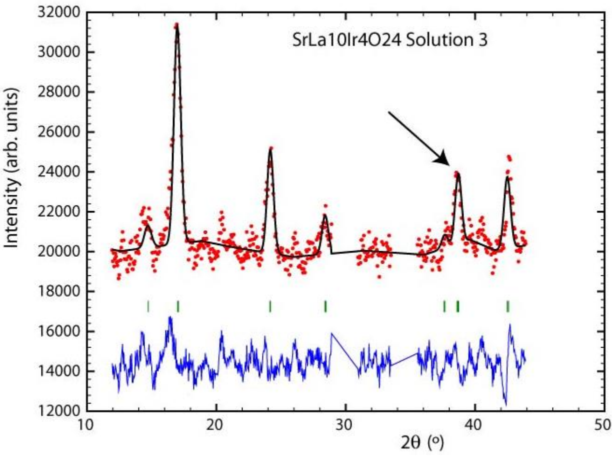
These figures show the analysis of the magnetic Bragg peaks (Left) and the resulting ground state magnetic structure (Right) corresponding to the solution 5

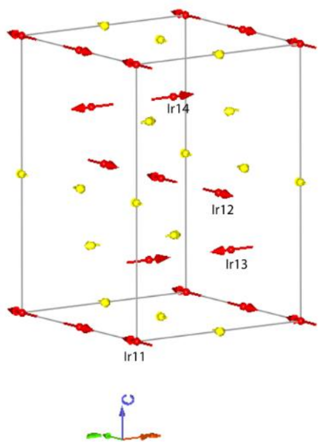
Ir_{11} on 0,0,0 and Ir_{12} on ¾,¼,¼ are parallel. Each of these creates another site where the magnetic moment is antiparallel. Each of the so created 4 sites is linked then through the I-centering to a further site. All these sites are in red in the figure. The yellow sites are the Ir2 sites: Ir_{21} on 0,0,½ and Ir_{22} on ¾,¼,¾ which are again parallel and create each one antiparallel site. Finally the I-centering is applied. Altogether, there are 8 Ir_1 and 8 Ir_2 sites in the unit cell.

Solution 3: R_{Mag} = 11.6, χ^2 = 19.6 , μ_{Ir1} = 0.60(1) μ_B, μ_{Ir2} = 0.21(1) μ_B or vice versa.

Magnetic moments in the tetragonal plane.

Only BV2 is used. BV1 does not work. Using BV3 additionally to BV2 leads to divergence.





The figures show the analysis of the magnetic Bragg peaks (Left) and the resulting ground state magnetic structure (Right) corresponding to the solution 3 using BV2.

The magnetic moments of the four sites are created by each of the two Ir1 & Ir2 are at 90° to each other, e.g. Ir_{11} at 0,0,0 is pointing along the *b*-direction, Ir_{13} points along (-*a*)-direction, Ir_{12} along the (-*b*)-direction and Ir_{14} along the *a*-direction. The I-centered sites are again parallel to the corresponding sites without I-centering. The Ir1 sites are shown by red arrows. The same order is present for the 8 Ir_2 sites which are shown in yellow and are at each layer height at 90° to the Ir1 sites positioned in the same layer.

Although R_{Mag} of solution 3 is lower than that of solution 5, one can't prefer this solution as the position of the refined magnetic Brag peak at 2Θ = 38.4° is slightly off in solution 3 (see arrow), while it is reasonable in solution 5 but it leads as well to the slightly increased χ^2 of solution 3. The difficulty to make a difference between the two solutions is attributed to the pseudo cubic lattice parameters: $\sqrt{2}a/c$ = 1.004 and to the fact that only the magnetic peaks at 2Θ = 14.7° and 28.4° have intensity differences between the two solutions and unfortunately, both of these two magnetic reflections are, however, low in intensity. So, to make a decisive comment one would need to perform additional magnetic measurements to have information on the easy axis direction.

$Sr_3La_8Ir_4O_{24}$ magnetic structure analysis: NPD was measured at the D20 instrument of ILL at two occasions at two different temperatures 15 K and 1.7 K: First for 8 hours, later again for 9.5 hours, with 42° Take-off angle and wavelength, λ = 2.415 Å.

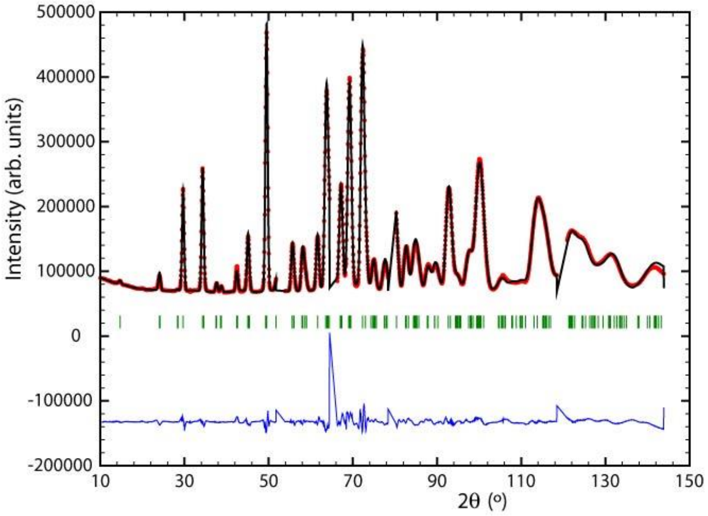
1) 15 K NPD: Both data sets were added to get better statistics: 17.5 hours total data collection time, Refinement was done using the atom coordinates and lattice constants obtained from the D2B 15 K structural characterization. The obtained scale factor from the D20 15 K data analysis is used for the magnetic structure refinement on the difference data file.

2) 1.7 K NPD: 8 hours + 9.5 hours, the two datasets were again added together.

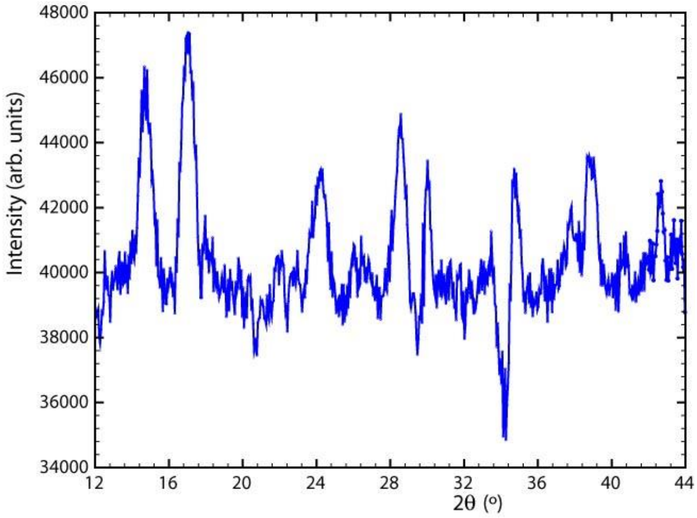
The added data from 15 K and from 1.7 K were used to create a difference data file: 1.7 K – 15 K +20000 which represents therefore the data file of,

1.7 K @17.5 hours – 15 K @17.5 hours.

These data were again smoothed to limit the statistical variations.



Refinement of the D20 data taken at 15 K on $Sr_3La_8Ir_4O_{24}$



Difference, 1.7 K – 15 K data from $Sr_3La_8Ir_4O_{24}$ collected on D20. Regions around 30° and 35° again were excluded from the refinements due to the up/down features of the nuclear Bragg peaks shifting with temperature.

All the magnetic Bragg peaks can be again indexed with the propagation vector k = 0. Therefore, the same three solutions as listed in the above table for $Sr_1La_{10}Ir_4O_{24}$ are allowed in case of $Sr_3La_8Ir_4O_{24}$.

A detail analysis on the magnetic structure determination of $Sr_3La_8Ir_4O_{24}$ is ongoing.