Experimental report

12/09/2024

Proposal: 5-41-1207 **Council:** 4/2023

Title: Magnetic structure evolution of the Nd2Ir2O7 pyrochore iridate through its field induced insulator to semimetal transition

Research area: Physics

This proposal is a new proposal

Main proposer: Quentin FAURE

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Local contacts: Eric RESSOUCHE

Samples: Nd2Ir2O7

Instrument	Requested days	Allocated days	From	To
D23	8	5	07/11/2023	12/11/2023
ORIENTEXPRESS	1	1	15/09/2023	16/09/2023

Abstract:

Pyrochlore iridates with formula A2Ir2O7 (A = rare earth) have attracted a lot of attention in the past decade due to comparable energy scales associated with crystal field, electronic correlations and spin-orbit coupling, which give rise to a very rich physics. Very recently, magneto-resistivity measurements performed on Nd2Ir2O7 showed that this material exhibits a field induced insulator to semimetal quantum phase transition around 10 T when the field is applied along the [100] direction. This intriguing transition is understood theoretically by the change of magnetic structure of the Nd sublattice from All-in-All-out (AIAO) to 2-in-2-out magnetic structure; the later affecting drastically the band structure of the Ir sublattice through f-d exchange coupling. While understood theoretically, this statement however, has not been confirmed experimentally. Our experiment intends to tackle this issue by performing a neutron diffraction experiment on an Nd2Ir2O7 single crystal under magnetic field.

Experimental report

Experimental title:	Magnetic structure evolution of the $Nd_2Ir_2O_7$ pyrochore iridate through its field induced insulator to semimetal transition
Proposal number:	**5-41-1207**
Instrument:	**D23**
Date of experiment:	7. – 12.11. 2023
Local contact:	Eric Ressouche
Experimental team:	Quentin Faure, Milan Klicpera, Elsa Lhotel, Sylvain Petit

Abstract:
Pyrochlore iridates with formula $A_2Ir_2O_7$ (A = rare earth) have attracted a lot of attention in the past decade due to comparable energy scales associated with crystal field, electronic correlations and spin-orbit coupling, which give rise to a very rich physics. Very recently, magneto-resistivity measurements performed on $Nd_2Ir_2O_7$ showed that this material exhibits a field induced insulator to semimetal quantum phase transition around 10 T when the field is applied along the [100] direction. This intriguing transition is understood theoretically by the change of magnetic structure of the Nd sublattice from All-in-All-out (AIAO) to 2-in-2-out magnetic structure, the latter drastically affecting the band structure of the Ir sublattice through f-d exchange coupling. While understood theoretically, this statement, however, has not been confirmed experimentally. Our experiment intends to tackle this issue by performing a neutron diffraction experiment on an $Nd_2Ir_2O_7$ single crystal under magnetic field.

Experiment and results:
The high-quality single crystal (0.7x0.7x0.7 mm^3, Fig. 1 and Fig. 2) was glued using epoxy to the aluminium sample pin with the [100] crystallographic direction aligned along the pin axis. Subsequently, the sample was inserted into the cryo magnet of the D23 diffractometer, again with the selected crystallographic axis aligned along the magnet's vertical axis.

Reachable nuclear reflections of the pyrochlore structure (*Fd-3m*, lattice parameter a = 10.3 Å) were calculated and searched for using the neutron wavelength of 2.41 Å. Surprisingly, low or no intensity was found on most of the calculated reflections. In contrast, some reflections calculated to be weak revealed a strong signal. All in all, spending one day aligning the single crystal using restricted possibilities of D23 equipped with cryo magnet (small opening of the magnet limited visible reciprocal space) led to two main conclusions:

(i) positive conclusion: the investigated single crystal, although of relatively small size, gives reasonable diffraction signal using D23 diffractometer. The investigation of, at least, nuclear structure is thus perfectly doable using neutron diffractometers.

(ii) negative conclusion: the crystal structure of the investigated single crystal is not pyrochlore structure with a = 10.3 Å. Instead, the lattice parameter of approximately 16.1 Å should be considered.

Indeed, an on-site single-crystal X-ray diffractometer subsequently confirmed the cubic lattice parameter of about 16.1 Å. However, inspecting the intensities of symmetry-related reflections of the cubic structure suggested a lower-symmetry structure, likely a tetragonal structure. High-statistics X-ray measurements done at the proposer's home institution on smaller single crystals (single crystals from the same synthesis batch and independent batches) allowed for refining the crystal structure. The space group of the structure was identified as tetragonal *I4/m*, and lattice parameters were refined to be a = 11.48 Å and c = 16.24 Å. Atomic positions of individual elements were also refined, leading to the structure depicted in Fig. 3. See the differences between the cubic pyrochlore and tetragonal structure there.

Of course, the refined atomic positions and especially their occupations are still ambiguous based on just the X-ray diffraction data. A neutron diffraction experiment is highly desirable to corroborate the X-ray

data, namely in accessing the oxygen positions and their occupations, which are not precise due to oxygen's small atomic number compared to Nd and Ir. Such neutron diffraction experiment is feasible, as proved by the D23 experiment.

In the following two days, we tested several single crystals on D23. Finally, a very small crystal of dimension approximately 0.01x0.01x0.01 mm^3 was successfully aligned and confirmed to adopt the pyrochlore structure with corresponding lattice parameter. We could measure the intensity of several nuclear reflections at room and base temperatures. Unfortunately, no clear difference in intensity was observed with varying temperatures (cooling below ordering temperature). Trialling to increase the statistics substantially (2 hours per point) did not improve the results. We highlight that the small crystal's volume was approximately 30 000 times smaller than that of the original large single crystal. With that and considering the magnetic intensity much smaller than the nuclear one, we concluded that continuing with the experiment was meaningless and allowed an internal use of the beam time.

Notice to the different crystal structure of the studied single crystal:

One could wonder why the different crystal structures of the investigated single crystal had not been identified before the experiment. Of course, the single crystal was characterized using several techniques: EDX to reveal the sample stoichiometry, Laue X-ray diffraction to prove the sample's single crystallinity and even specific heat and magnetization measurements. None of the techniques showed any difference from previously studied powder samples. Importantly, a bifurcation of ZFC and FC magnetization, indicating the magnetic phase transition, was observed at 39 K for the investigated single crystal. This is the highest reported value for a single crystal and the same value reported for polycrystalline samples. Such an observation is very important because the same magnetic properties were revealed for pyrochlore polycrystal and tetragonal single crystal!

We admit that the single crystal X-ray diffraction was not performed before the neutron experiment on the investigated sample. Since then, we have also tested other single crystals of the same shape, size, and quality, e.g., $Ho_2Ir_2O_7$, $Er_2Ir_2O_7$, and $Lu_2Ir_2O_7$, synthesized by the same method. The ordered pyrochlore structure with respective lattice parameters was identified in all these crystals by the same single crystal X-ray diffractometer. The different crystal structure of the $Nd_2Ir_2O_7$ single crystal is, therefore, highly interesting and is bound to be crucial for properly interpreting the electronic properties of light rare-earth iridates.

We intend to propose a continuing experiment to determine the crystal structure unambiguously and, in turn, re-investigate the magnetic structure of this compound. Our tetragonal single crystal cannot realise the previously reported AIAO antiferromagnetic ordering for pyrochlore powder samples.

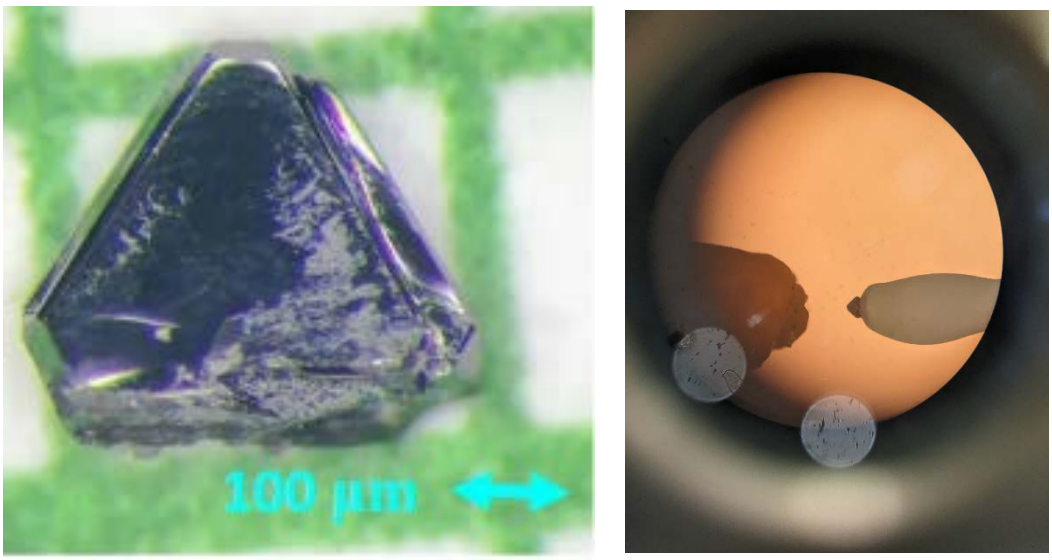

Fig.1 – $Nd_2Ir_2O_7$ single crystal studied using the D23 diffractometer. Picture of the free single crystal and crystal mounted on the sample holder.

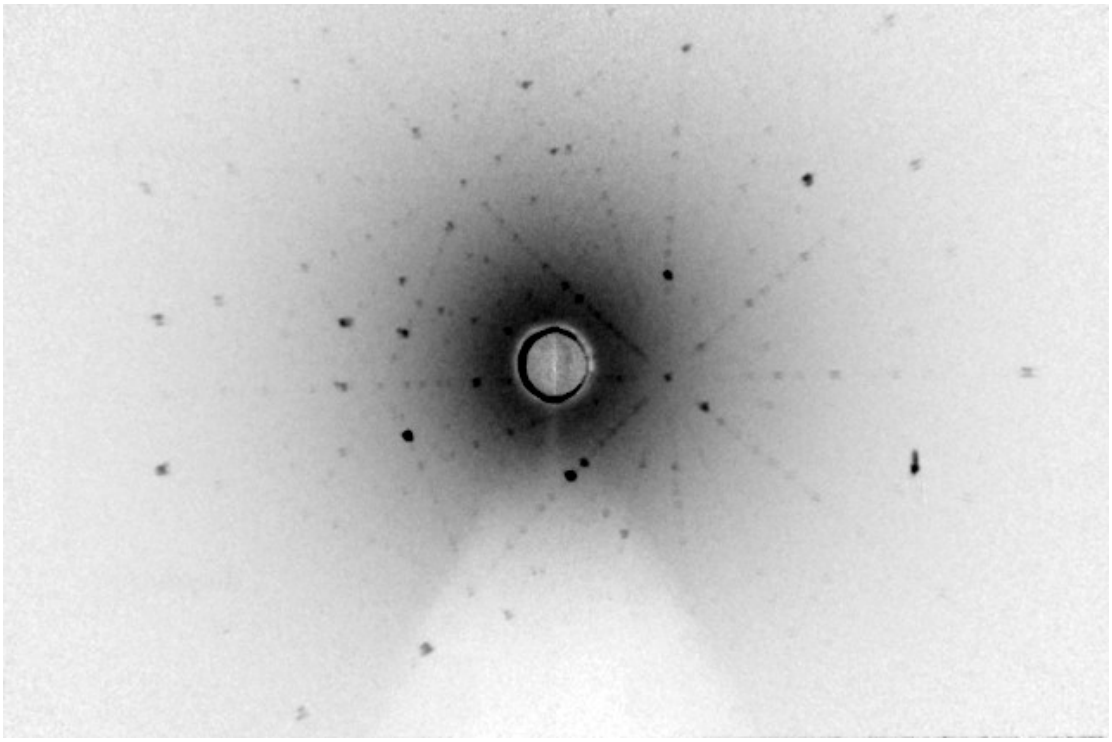

Fig.2 – Laue X-ray diffraction patterns of $Nd_2Ir_2O_7$ single crystal. The good quality of the crystal is demonstrated.

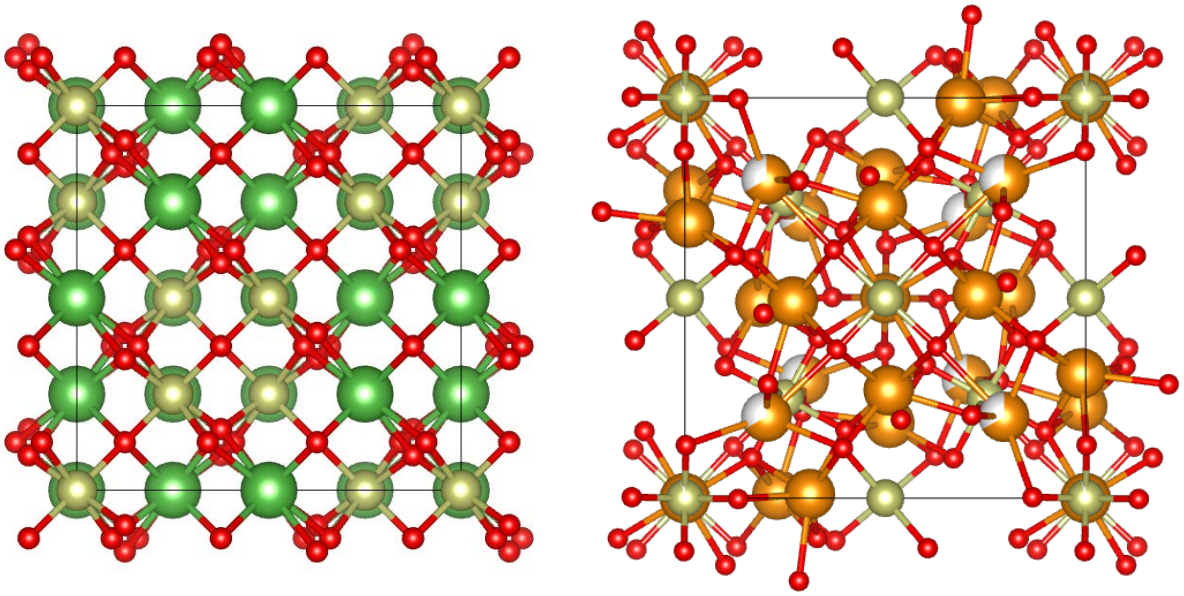

Fig.3 – Unit cell of the pyrochlore type of cubic structure and proposed tetragonal structure (the same size of cell is used for better comparison with pyrochlore lattice).