Experimental report

08/08/2023

Proposal: 5-31-2940 **Council:** 10/2022

Title: Probing the ground state magnetic structures of LiNi(1-x)Fe(x)PO4.

Research area: Physics

This proposal is a new proposal

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Samples: LiNi(1-x)Fe(x)PO4 x=0.1, 0.3, 0.5, 0.7, 0.9
Li(Co,Ni)PO4, x=0, 0.15, 0.30, 0.50, 0.75

Instrument	Requested days	Allocated days	From	To
D1B	3	3	19/05/2023	22/05/2023
D2B	2	2	14/04/2023	16/04/2023

Abstract:

We propose to detemine the crystal and magnetic structures for selected compositions within the family, LiNi(1-x)Fe(x)PO4, of antiferromagnetic magnetoelectrics. With respect to the magnetic structures found at low temperatures, the proposed experiment will test existing predictions from our own Monte Carlo simulations.
The expected results will feed into the longer-term plan of this ILL PhD project, by allowing us to identify the best compositions for single-crystal growth and further explorations of the link between magnetic structures and magnetoelectric properties.

Determining the magnetic structures of $LiCo_{1-x}Ni_xPO_4$

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Introduction

Lithium orthophosphates ($LiMPO_4$ M=Fe, Ni, Co, Zn) are a family of olivine-structured (Space group Pnma) antiferromagnets that display a magnetoelectric effect below their respective ordering temperatures [1]. These compounds differ from each other only in the direction along which the magnetic moment aligns. The components of the magnetoelectric tensor (the tensor which connects the applied magnetic field with the induced electric polarisation and vice versa P=α H) are determined by the symmetry of the magnetic structure [1]. Magnetic point groups which allow off-diagonal asymmetric magnetoelectric tensor elements also allow a ferrotoroidal moment to exist [2]. In $LiCoPO_4$ and $LiNiPO_4$ the magnetic moments align mainly along the b and c axis respectively [3,4]. The symmetry of their magnetic structure allows nonzero off-diagonal magnetoelectric tensor elements which makes them potential candidates for the ferrotoroidic ordering. In the past, ferrotoroidic order has been successfully observed in $LiCoPO_4$. In $LiCoPO_4$, small canting of the magnetic moment towards the c axis and the finite displacement of transition metal ions from the face-centered position inside the crystal are two factors that influences the existence and magnitude of ferrotoroidic ordering [3]. Since the canting of magnetic moment towards the c axis influence the magnitude of ferrotoroidal moment, changing the canting angle could be a potential way to tailor the ferrotoroidic order. Since in $LiNiPO_4$ Ni ions prefer to align along the c axis, substituting random Co ion sites in $LiCoPO_4$ with Ni ions results in a change in canting angle by acting as an internal c axis field. This could in turn change the toroidal moment. In this experiment, we proposed to observe the changes in the magnetic structure with substitution ratio x in $LiCo_{(1-x)}Ni_xPO_4$ to determine the composition dependence of the canting angle.

Experimental setup

Crystal and ground state magnetic structure of the 5 samples $LiCo_{(1-x)}Ni_xPO_4$ (x= 0, 0.15, 0.3,0.5,0.75) were probed using the instruments D2B and D1B. At D2B The powder diffraction data were collected at 3 different temperatures 5 K, 50 K, and room temperature using the wavelength 1.594 Å. At D1B, neutron diffraction data were collected at 2 different wavelengths 1.26 and 2.52 Å . Data was collected at 2 K and 50 K. To get information on the temperature dependence of the magnetic structure, data were collected at different temperatures by varying the temperature from 2 K to a few Kelvin above the ordering temperature

Results

From the powder neutron data, it was confirmed that all 5 of the samples crystallize in the orthorhombic olivine crystal structure (space group Pnma) and the occupancies of Ni and Co ion on the transition metal site of the crystal was refined which confirmed the nominal concentrations.
The powder diffraction data showed a change in the magnetic structure with composition. For the compounds with x=0, 0.15, and 0.3 an antiferromagnetic structure with irreducible representation Γ_4 matched the observed diffraction pattern in which the magnetic moments are aligned predominantly along the b axis. Whereas for x=0.5 the combination of $\Gamma_4 + \Gamma_6$ gave the best agreement with the observed pattern in which the magnetic moment has a component along the c axis. For x=0.75, the magnetic structure represented by Γ_6 produced the observed diffraction pattern where the magnetic moment is aligned mainly along the c axis. This change in magnetic structure is visible from the considerable intensity observed at (010) peak from x=0.5 onwards (Fig. 1). The

ordering temperatures for all the compounds were confirmed using the diffraction data collected by varying temperatures.

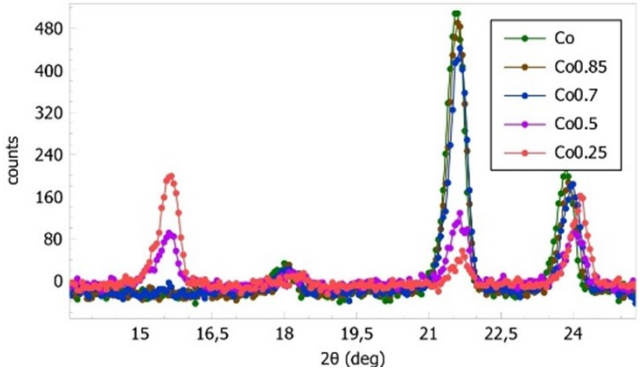

Figure 1: Magnetic diffraction patterns of $LiCo_{(1-x)}Ni_xPO_4$ for x=0, 0.15, 0.3, 0.5, 0.75. There is a new peak arising around 16° for x=0.5 and x=0.75

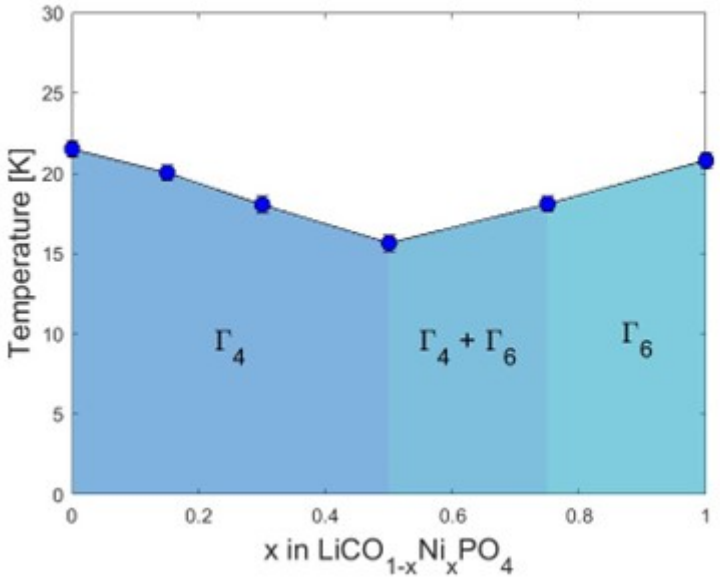

Figure 2: Phase diagram with data points representing ordering temperature from D1B data and the change in magnetic structure denoted by corresponding irreps.

References

1. J.-P. Rivera, Eur. Phys. J. B **71**, 299-313 (2009)
2. S. Gnewuch, E. E. Rodriguez, J. Solid State Chem 271, 175 (2019)
3. B. B. Van Aken et al, Nature 449, 702 (2007)
4. T. B. S. Jensen et al, Phys. Rev. B. 79, 092412 (2009)