Experimental report

25/01/2024

Proposal:	**5-31-2974**	**Council:**	4/2023

Title: Determining the magnetic structures of LiCo(1-x)Ni(x)PO4

Research area: Physics

This proposal is a new proposal

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Samples: LiCo(1-x)Ni(x)PO4 x=0, 0.15, 0.30, 0.5, 0.75

Instrument	Requested days	Allocated days	From	To
D2B	2	2	05/09/2023	08/09/2023
D20	3	2	04/09/2023	06/09/2023
D1B	3	0		

Abstract:

LiCoPO4 is known to exhibit ferrotoroidic order as a result of two specific aspects of its crystal and magnetic structure: A displacement of the Co2+ ions away from high-symmetry positions, and canting of the magnetic moments away from the b-axis towards the c-axis. We
conjecture, that when Ni2+ ions replace Co2+, they act as internal c-axis fields, increasing the canting angle, and modifying the ferrotoroidic moment. To test this hypothesis, we propose to determine the crystal and ground state magnetic structures of five powder samples spanning from LiCoPo4 to LiCo(1/4)Ni(3/4)PO4.

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 that connects the applied magnetic field with the induced electric polarisation and vice versa $P=\alpha H$) are determined by the symmetry of the magnetic structure [1]. Magnetic point groups which al low 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 influence the existence and magnitude of ferrotoroidic ordering [3]. Since the canting of magnetic moment towards the c axis influences the magnitude of the 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 the 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 were 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 Γ_4 + Γ_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.

However, we were not able to observe any intensity for the peak corresponding to 010 for LiCoPO4, which has been reported previously by Vaknin et al [5], indicating the small canting of magnetic moment towards c - axis. But the magnetic structure represented by the combination of gave an equally good fit to the observed diffraction pattern with a very small spin rotation towards the c axis. Consequently, there remains some ambiguity in the magnetic structure, requiring further dedicated investigation.

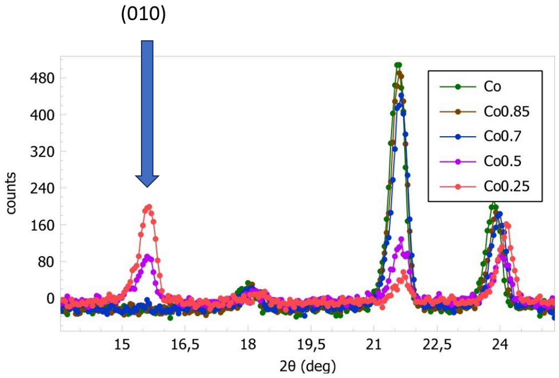

Figure 1: Magnetic diffraction patterns of $LiCo_{(1-x)}Ni_xPO_4$ for x=0, 0.15, 0.3, 0.5, 0.75. There is a new peak arising around 16° for x=0.5 and x=0.75

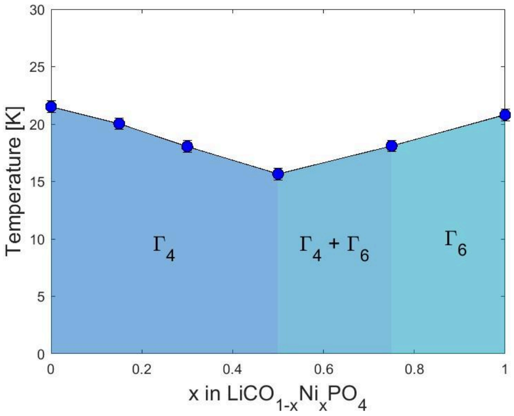

Figure 2: Phase diagram with data points representing ordering temperature from D1B data and the change in magnetic structure denoted by corresponding irreps.

References

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