Experimental report

19/10/2018

Proposal:	**5-31-2590**	**Council:**	4/2018
Title:	Crystal and magnetic structures ofnew spinel type phases		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: Co4FeSbO8
Co4MnSbO8
Co2Cr3GaO8

Instrument	Requested days	Allocated days	From	To
D2B	2	1	11/09/2018	12/09/2018
D1B	2	1	10/09/2018	11/09/2018

Abstract:

As part of Stanislav Podchezertsev's thesis (in co-direction between CRISMAT and ILL) we started to study new ordered spinel phases Co5-xZnxTeO8. We particularly interested in polymorphic phases Co5TeO8: the disordered phase (centrosymmetric Fd-3m) and the ordered phase (non-centrosymmetric P4332). For this latter, short-range magnetic domains appear below 60 K followed by the emergence of an incommensurate conical-spiral magnetic ordering below 50 K which allows magnetoelectric coupling. The behavior only exists in the ordered phase. Thus, the search of new ordered spinels is of interest to find new magnetoelectric materials. In this context, we synthesized polycrystalline samples of Co4FeSbO8, Co4MnSbO8, Co2Cr3GaO8. Until now, we only obtained the disordered phases. Nevertheless, preliminary SQUID measurements show interesting magnetic behaviors with several magnetic transitions. We need neutron diffraction data to characterize the magnetic transitions, the crystal and magnetic structures of these disordered phases. These studies are essential to evidence the driving forces which allow the appearance of the magnetoelectric coupling in the ordered spinel phases.

Experiment 5-31-2590

Crystal and magnetic structures of new spinel type phases

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Introduction

Spinel phases are compositions with general chemical formula AB_2X_4, where A and B are transition metal ions and X are oxygen or chalcogens, with a cubic *Fd-3m* structure. Within this structure A-site cations have tetrahedral surrounding whereas B cations occupy the octahedral site. Recently it was discovered that several spinel phases can possess type-II multiferroic behaviour. One of the examples is $CoCr_2O_4$ which demonstrates complex reentrant magnetic ground state below 13 K preceded by two magnetic phase transitions: collinear ferrimagnetic appearing at 93 K followed by incommensurate spiral ordering below 27 K [1]. With an absence of any structural phase transitions at low temperatures, centrosymmetry is locally broken by a spiral ordering and electrical polarization occurs below 27 K [2]. Thus the potential discovery of novel spinel phases exhibiting strong magnetoelectric coupling attracts significant attention. Within the current project, we were investigating nuclear and magnetic structures of three new spinel compounds Co_4MnSbO_8 ($Co_2Mn_{0.5}Sb_{0.5}O_4$), Co_4FeSbO_8 ($Co_2Fe_{0.5}Sb_{0.5}O_4$) and $Co_2Cr_3GaO_8$ ($CoCr_{1.5}Ga_{0.5}O_4$).

Experimental

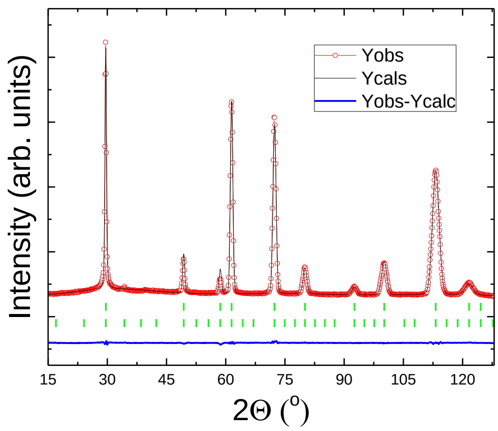
For diffraction measurements, samples of around 5g each were packed into vanadium cylindrical containers with an inner diameter of 8mm. To probe nuclear structures of studied compounds at various temperatures D2B powder diffractometer was used with a wavelength $\lambda = 1.59$ Å and diffraction patterns were collected in the angular region 2θ between 0^o and 160^o. For each sample three diffraction patterns with good statistics at different temperatures were measured: 1,5K, 100K and 300K. To characterize magnetic structures we used the D1B diffractometer with an incident wavelength $\lambda = 2.52$ Å. For each sample diffraction pattern with good statistics were collected at 1.5 K with a consequential heating to 300 K and measurement of patterns with a temperature step of 5K. To regulate the temperature at both D1B and D2B instruments orange cryostats were used.

Preliminary results

Neutron powder diffraction has confirmed classical cubic *Fd-3m* structure for each studied sample. For $Co_2Cr_3GaO_8$ compound combined neutron and X-ray Rietveld refinements haven't shown any intermixture between Co and Cr occupying tetrahedral and octahedral sites respectively while for both Co_4MnSbO_8 and Co_4FeSbO_8 tetrahedral and octahedral sites are partially occupied by Co and Mn/Fe. Low-temperature neutron diffraction data revealed that all three samples undergo a ferrimagnetic phase transition. The magnetic structures were refined from neutron diffraction data recorded at 1.5 K. The Neel temperature T_N and the magnetic moments for both A- (tetrahedral) and B- (octahedral) sites are shown in the following table.

Table 1. Neel temperature and magnetic moment for both tetrahedral and octahedral sublattices

Composition	T_N (K)	$\mu_{A\text{-site}}$ at 1.5K (μ_B)	$\mu_{B\text{-site}}$ at 1.5K (μ_B)
Co_4MnSbO_8	84	2.190(22)	-2.719(27)
Co_4FeSbO_8	215	2.342(54)	-1.934(65)
$Co_2Cr_3GaO_8$	80	3.179(67)	-4.062(94)



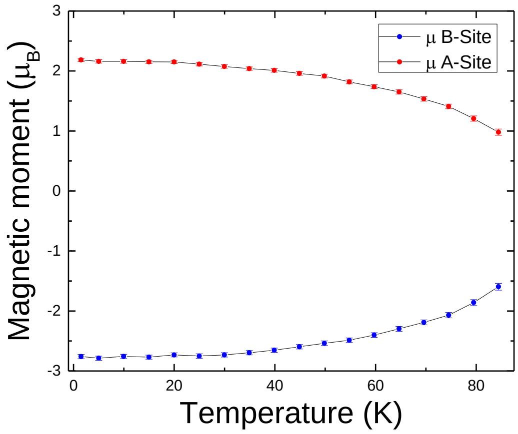


Fig. 1 Rietveld refinement of Co_4MnSbO_8 magnetic structure from D1b data recorded at 1.5K

Fig 2. Temperature evolution of magnetic moments at A and B-sites of Co_4MnSbO_8

Moreover for $Co_2Cr_3GaO_8$ neutron diffraction at low temperatures revealed emergence of diffuse scattering centered at a higher angles (~35°2θ) regarding to fundamental (111) reflection, (Fig. 3) pointing out to a presence of additional short-range correlations which, in turn, could indicate that ferrimagnetic phase is not the ground state of the studied system.

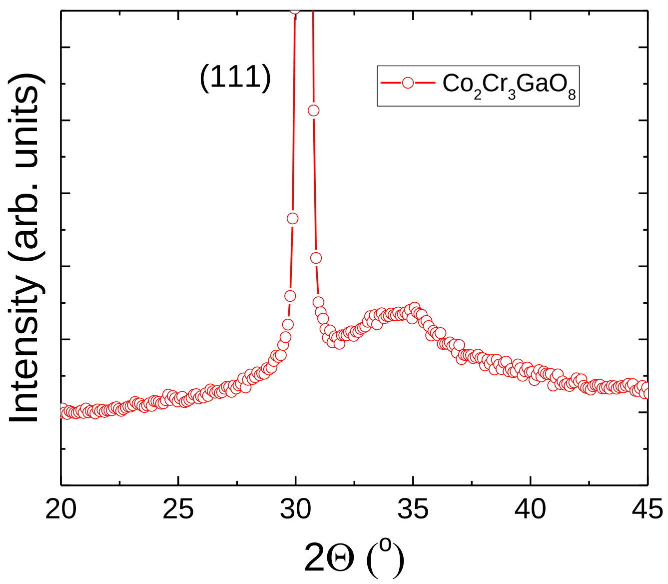


Fig. 3 Fragment of $Co_2Cr_3GaO_8$ diffractogram at 1.5 K showing the presence of a diffuse magnetic peak

Bibliography

[1] Tomiyasu, et al. (2004) *Physical Review B*, *70*(21), 214434.
[2] Yamasaki et al. (2006). *Physical review letters*, *96*(20), 207204.