Experimental report

16/07/2021

Proposal: **5-31-2803** **Council:** 4/2020

Title: Spin lattice coupling and frustration in ZnCr2Se4 spinel

Research area: Physics

This proposal is a new proposal

Main proposer: **Nicolas MARTIN**

Experimental team:

Local contacts: Claire COLIN

Samples: ZnCr2Se4

Instrument	Requested days	Allocated days	From	To
D1B	1	1	17/08/2020	18/08/2020

Abstract:

Cr-spinels with formula ZnCr2X4 (X = O, S, Se) are nice playgrounds to study spin frustration under the influence of spin-lattice coupling. In ZnCr2Se4, a helimagnetic (HM) ground state is stabilized below TN = 21 K, as a result of a competition between nearest-neighbor (NN) antiferromagnetic Cr-Cr direct exchange and next-NN ferromagnetic super-exchange. Applying pressure is an efficient way to tune this interaction scheme. Using the G6.1 (LLB), DMC (PSI) and D20 instruments, we have followed the suppression of the HM long-range order and have found that it collapses at P ~ 7 GPa. Concomitantly, it is gradually replaced by a partially-ordered (PO) phase with a low moment but very high TN (larger than 300 K), surviving up to the largest pressures (~ 9 GPa). In order to clarify the origin of this PO phase and get a solid basis for the analysis of our high-pressure data, we need to record ambient pressure PND patterns of our ZnCr2Se4 sample in the 1.5-300 K range. This will allow us determining the HM critical behavior (in the region of TN) and search for traces of diffuse scattering, precursor to the PO phase, between TN and the transition to a fully paramagnetic state.

Experimental report for proposal 5-31-2803
"Spin lattice coupling and frustration in $ZnCr_2Se_4$ spinel"

The purpose of the experiment was an accurate study of the ambient pressure magnetic structure of two $ZnCr_2Se_4$ samples, issued from different synthesis. Both were previously studied using neutron powder diffraction (NPD) under moderate (DMC@SINQ-PSI and G61@LLB) and high pressures (D20@ILL). In order to prepare the D1B experiment, we have used X-ray powder diffraction and susceptibility measurements to obtain more information on the structural and magnetic properties of our samples. These studies revealed that the so-called "X" impurity phase, known to be present in both samples, could be consistent with the $Ba_{1-x}Sr_xZnFe_6O_{11}$ ferrite. It crystallizes in the R-3m space group and presents a helimagnetic character with high temperature ordering[1].

Thanks to the high flux of the ILL reactor, we have been able to acquire temperature-dependent NPD patterns with sufficient statistics through constant ramps (2 K < T < 300 K, ≈ 0.3 K/min) on both samples, further called "PSI" and "D20". Importantly, the instrumental resolution allowed resolving **for the first time**, the overlapping small angle magnetic contributions of the $ZnCr_2Se_4$ and "X" phases (**Fig. 1**).

In the D20 sample, the low-T NPD patterns were refined by involving 4 phases, namely $ZnCr_2Se_4$ nuclear (N) and magnetic (M) (phases #1 and #2), and "X" N and M (phases #3 and #4). The amount of the "X"-phase was here evaluated to 13(2) %. The analysis showed unambiguously that a magnetic contribution due to the helical satellite $(003)^-$ from the "X"-phase is superimposed on the $(000)^+$ magnetic satellite of the $ZnCr_2Se_4$ helical structure (**Fig. 1, Left**). When the temperature increases, the $(000)^+$ satellite of $ZnCr_2Se_4$ vanishes at $T_N \approx 17.9$ K, whereas that of the "X"-phase vanish at much higher temperature, close to ≈ 294 K (**Fig. 2**). This is an important result, since the high temperature signal observed above T_N in the high-pressure D20 data could not be identified up to now.

In the PSI sample, the low-T NPD patterns were refined by involving 6 phases, namely 3 nuclear (phases #1, #3 and #5) and their magnetic counterparts (phases #2, #4 and #6). They correspond to $ZnCr_2Se_4$ spinels with slightly different lattice constants, coexisting with the X-phase. The relative amounts are 54(5) % (spinel phases #1 and #2, a = 10.466(5) Å, $T_N \approx 17.3$ K), 41(4) % (spinel phase #3 and #4, a = 10.489(7) Å, $T_N \approx 21.5$ K), and 5(1) % ("X"-phase, phases #5 and #6, $T_N \approx 282$ K) (**Fig. 3**)

Conclusions – The experiment proved crucial to interpret our previous high-pressure data on a safe basis, by providing a clear interpretation of the high temperature signal observed above T_N at the position of the $(000)^-$ satellite of the $ZnCr_2Se_4$ helical structure. It also showed that, at ambient pressure, the Néel temperature strongly depends of the lattice constant. The smaller T_N corresponds to the sample with the smaller lattice constant, underscoring the importance of spin-lattice coupling in this system (**Fig. 4**). This also agrees with high-pressure measurements, showing that T_N decreases under pressure.

[1] J. Muller *et al.*, JMMM **102** (1991) 305-313

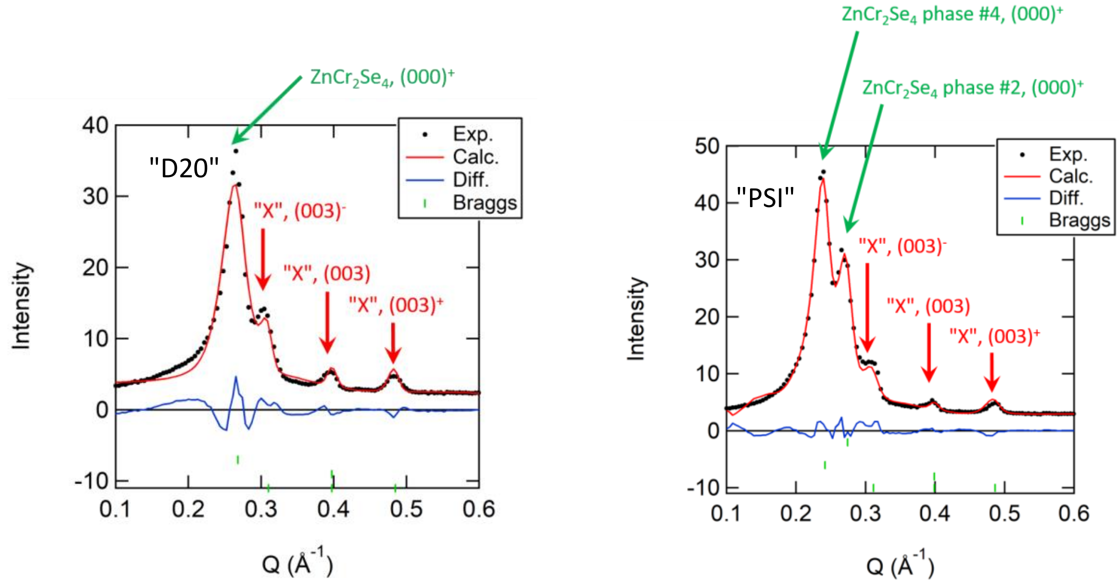

Fig. 1 – Small-angle part of the diffraction patterns obtained during the experiment, showing the various magnetic contributions. **Left:** On the "D20" sample. **Right:** On the "PSI" sample.

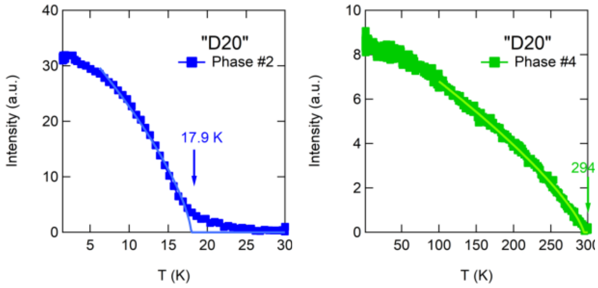

Fig. 2 – Temperature-dependence of the magnetic $(000)^+$ Bragg intensities in the "D20" sample. **Left:** $ZnCr_2Se_4$ magnetic phase. **Right:** "X" magnetic phase.

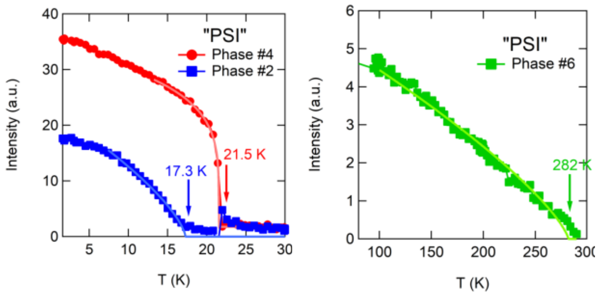

Fig. 3 – Temperature-dependence of the magnetic $(000)^+$ Bragg intensities in the "PSI" sample. **Left:** $ZnCr_2Se_4$ magnetic phases. **Right:** "X" magnetic phase.

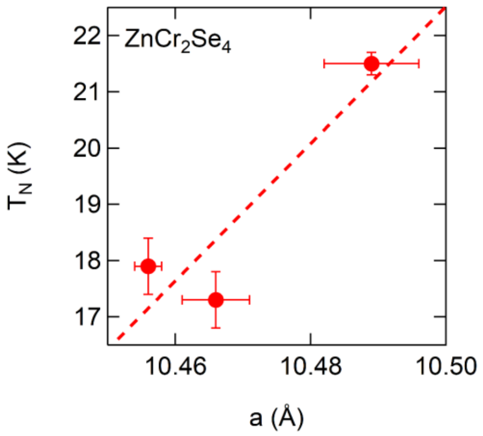

Fig 4 – Dependence of the Néel temperature (T_N) on the cubic lattice constant (*a*) of $ZnCr_2Se_4$.