Experimental report

05/09/2019

Proposal:	**5-31-2610**	**Council:**	4/2018
Title:	Spin Structure and Na-ion Diffusion in NaCrTe2		
Research area:	Physics		

This proposal is a new proposal

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Samples: NaCrTe2

Instrument	Requested days	Allocated days	From	To
D2B	4	3	05/10/2018	08/10/2018

Abstract:

The aim of the experiment here proposed would be to characterize the atomic structure and the spin structure of the novel compound NaCrTe2 as a function of temperature. This material has been studied by our sample provider using x-ray powder diffraction and bulk magnetic measurements, from which is evident that it has a peculiar spin structure consisting of antiferromagnetically coupled ferromagnetic layers. Moreover, NaCrTe2 could be a good candidate as a cathode material in batteries because of its atomic structure, very similar to many of the most used battery cathode materials (LiCoO2). To probe the goodness of NaCrTe2 as battery material it is necessary to study the Na-ion diffusion within the layers so, since currently the structural transitions and ion-dynamics around room-temperature in NaCrTe2 is an unexplored field, we aim to investigate this aspect too. The NaCrTe2 has, to the best of our knowledge, never been studied by neutron diffraction so we believe that further efforts should be put in this direction.

Background and Context

Two dimensional triangular-lattice compounds (2DTL) exhibits a variety of intriguing physical properties. In particular, we are interested in the magnetic properties of chromium compounds, that are affected by a particular geometry of the crystal structure. CrTe2 is a metallic S=3/2 compound where the Cr ions create the 2DTL structure by the connection of edge-sharing CrTe6 octahedra [see Fig. 1 (a) and (c)].

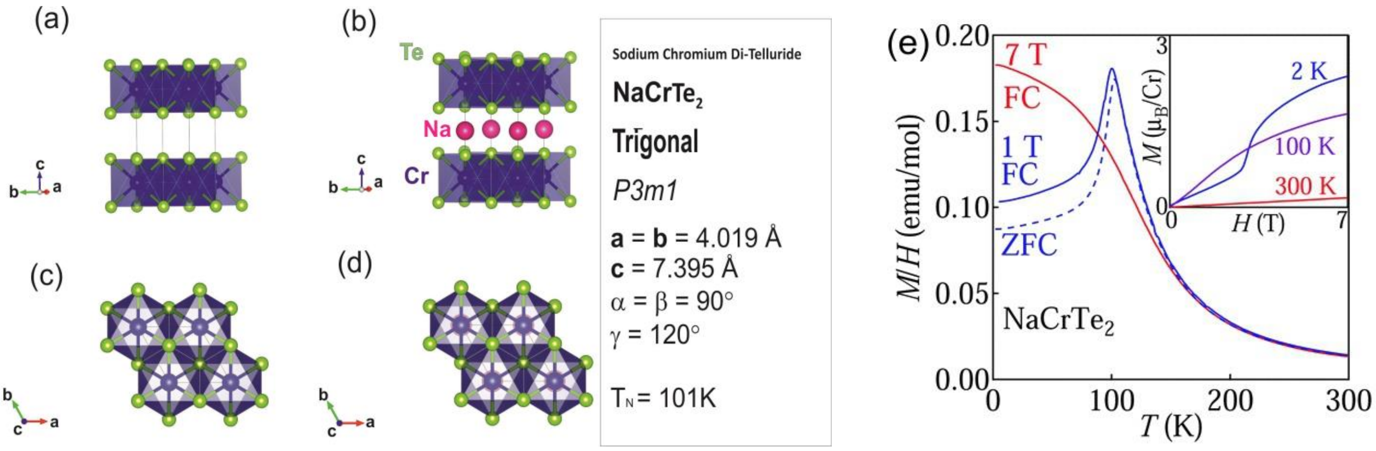

Fig. 1. *Crystal structure of (a) CrTe2 and (b) NaCrTe2. View along the crystallographic c-axis for (c) CrTe2 and (d) NaCrTe2, which shows the two-dimensional triangular lattice (2DTL) of the Cr atoms. (e) Magnetic susceptibility of NaCrTe2 under 1T and 7T external fields. The inset shows the magnetization for different temperatures*.

Na+ ions insertion into the CrTe2 crystal structure, has led to the synthesis of a novel compound: the NaCrTe2 [Fig. 1 (b) and (d)]. The latter has been investigated by our sample provider by means of x-ray powder diffraction and bulk magnetic susceptibility measurements [Fig. 2]. The latter shows the appearance of a magnetic ordering, evidenced by the cusp at T_N = 101K which indicates the occurrence of an antiferromagnetic transition. This, together with the large value of the Curie-Weiss temperature Θ = 140K (indicating that the ferromagnetic interaction is dominant within a layer), has led to the conclusion that $NaCrTe_2$ consists of antiferromagnetically coupled ferromagnetic layers. For this reason, we wanted to explore the spin structure of the NaCrTe2 as a function of temperature. Moreover, NaCrTe2 could be a good candidate as a cathode material in batteries, because of its layered crystal structure with the Na-ion planes sandwiched between the CrTe2 planes [Fig. 1 (b)]. Such structure is very similar to many of the current battery cathode materials e.g. LiCoO2, and NaCoO2. In particular, detailed analysis made within our collaboration on the latter compound by neutron powder diffraction, indicate the existence of two first-order structural transitions that are related to the onset of Na ion diffusion. Currently the structural transitions and ion-dynamics around room-temperature in NaCrTe2 is an unexplored field. Therefore, it will also be very interesting from the view-point of the applications in the sustainable energy materials framework.

The Performed Experiment

The aims of the proposed experiment were the following: 1) deduce the low temperature spin structure of NaCrTe2; 2) characterize subtle structural transitions and possible signature of Na-ion diffusion around room temperature. For these two purposes we performed a neutron powder diffraction experiment at the diffractometer D2B.

As a starting point we were mainly interested in the "static" properties: spin order, atomic structure and transitions. Here, we believe the antiferromagnetic interlayer interaction is governed by Na ordering within the layers. Therefore, our aim was to study order/disorder within the Na-ion planes. The experimental plan was to first acquire 2 high-statistic diffraction patterns (below and above TN, and at base-temperature T = 2K) to discern any magnetic Bragg peaks. Further, we would have followed the magnetic order parameter by acquiring several scans as a function of temperature, following the intensity of the magnetic peaks.

For the high temperature study of the atomic structure our aim was to investigate the appearance of subtle structural transitions around the onset temperature of ion diffusion (Tdiff ≈ 150K, estimated from previous measurements on a similar sample). We know that we could potentially expect the main changes within the metal-ion planes i.e. here in the Na-planes. For this purpose, we planned to record diffraction patterns as a function of temperature in the range T=50-450K, in steps of 20K.

Results

During the calibration for the choice of the wavelength (2.39Å) the signal looked anomalously weak [Fig. 2 (blue pattern)]. Our suspect is that the sample was partially decomposed due to oxygen contamination in the glovebox we used at the ILL site. This is because the sample was fine before the ILL experiment as evidenced by the XRD pattern collected by our sample provider. Attempts of peak indexing with the Le Bail method evidenced a big difference between the reported crystal structure for NaCrTe2. After the calibration we had problems with the cryostat: the He level dropped dramatically and the sample heated up to 100K from the base temperature during the measurement. The reason for this was that the cryostat could not keep the insulating vacuum, and the He was in thermal contact with the outside ambient environment. As a consequence, the He was continuously evaporating during the measurement. In the attempt of fixing the cryostat, the ILL staff took out the sample at 100K, the thermal shock caused the breaking of the vacuum in the sample holder (5mm vanadium cell with helicoflex type sealing) which caused further decomposition of our sample [Fig. 2 (red pattern)]. Finally the cryostat problems continued even further and we had to change the sample environment completely, again causing the thermal cycling and air leaking into the sample can. In summary, this experiment was unfortunately not successful due to a series of technical problems at ILL.

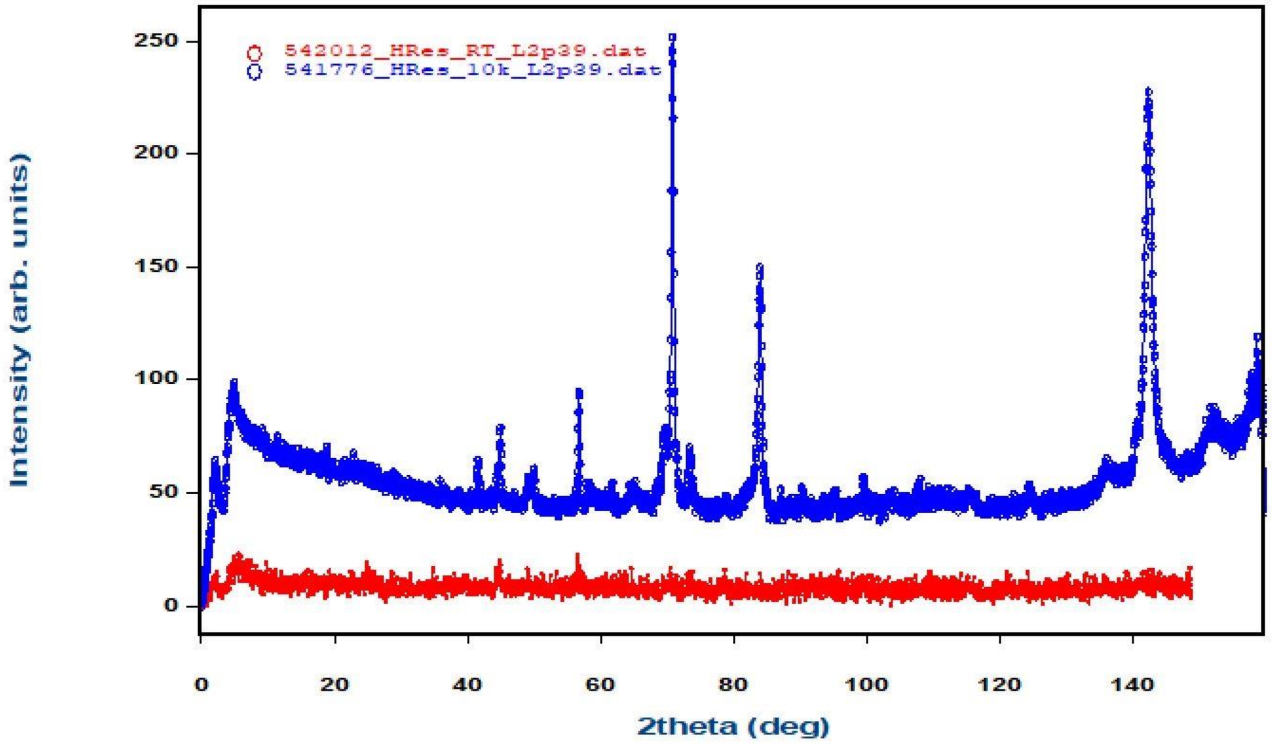

Fig. 2 *Diffraction patterns for NaCrTe$_2$ at 10K before complete decomposition (blue) and at room temperature after complete decomposition (red).*

References

[1] S. Kobayashi, et al. Inorganic Chemistry **55**, 7407 (2016).	[4] M. Medarde et al. Physical Review Letters **110**, 266401 (2013).
[2] E. Antolini, Solid State Ionics **170**, 159171 (2004).	[5] Jun Sugiyama, et al. (2017), Accepted for Publication.
[3] J. Sugiyama *et al:*, (2017), unpublished.	