# Experimental report

15/02/2022

**Proposal:** **5-31-2795**

**Council:** 4/2020

**Title:** Crystal and magnetic structure of Howardevansite and its candidate multiferroic Li analogue

**Research area:** Physics

**This proposal is a new proposal**

**Main proposer:** **Sebastian BIESENKAMP**

**Experimental team:**

**Local contacts:** Thomas HANSEN

**Samples:** $LiCuFe_2(VO_4)_3$
$NaCuFe_2(VO_4)_3$

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D1B | 2 | 1 | 03/09/2020 | 04/09/2020 |
| D2B | 2 | 2 | 01/02/2021 | 03/02/2021 |

## Abstract:

Both systems, $NaCuFe_2(VO_4)_3$ , and its analogue, $LiCuFe_2(VO_4)_3$ , crystallize in the triclinic space group P-1. It is the lowest possible symmetry allowing for a multiferroic transition and indeed, the dielectric constant of the Li compound exhibits a strong peak, while there is no dielectric anomaly for the Na compound. The entity of information for $LiCuFe_2(VO_4)_3$ suggests a multiferroic state with a possibly different mechanism of multiferroic coupling. We therefore propose to study the nuclear and magnetic structures of the two materials, $NaCuFe_2(VO_4)_3$ and $LiCuFe_2(VO_4)_3$ , by powder neutron diffraction on the D1B and D2B diffractometer.

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**Both related systems, $NaCuFe_2(VO_4)_3$ and $LiCuFe_2(VO_4)_3$ crystallize in the triclinic space group P-1, which is the lowest possible symmetry for a system to develop multiferroic behavior. Indeed, the dielectric measurements of the Li compound revealed a strong peak simultaneous to the onset of magnetic ordering. In contrast, no dielectric anomaly was reported for the related Na compound. Recent results suggest that the potential multiferroic state in $LiCuFe_2(VO_4)_3$ is of different nature compared to other typical type-II multiferroics. We, therefore, proposed to study the nuclear and magnetic structures of the two materials, $NaCuFe_2(VO_4)_3$ and $LiCuFe_2(VO_4)_3$, by powder neutron diffraction on the D1B and D2B diffractometer.**

The mineral Howardevansite, $NaCuFe_2(VO_4)_3$, and its analogue, $LiCuFe_2(VO4)_3$, crystallize in the triclinic space group P-1 [1-3], with $a$ = 8.15 Å, $b$ = 9.80 Å, $c$ =6.64 Å, $\alpha$ = 104°, $\beta$ = 102°, and $\gamma$ = 107° for Li [3]. The Cu ion is two-valent with an expected spin of ½, Fe is three-valent with S=5/2 and V is 5+ and thus nonmagnetic in these materials. Magnetism is hence arising from two different 3d metals that are arranged in complex zigzag chains. The magnetic susceptibility of the two compounds shows kinks indicating two successive magnetic transitions for the Li as well as for the Na compound [4,5]. For Li at $T_1$=9.8K and $T_2$=8.2K. For Na at $T_1$=9.3K and $T_2$=5.2K.

Two successive magnetic transitions are frequently observed in multiferroics and indeed the dielectric constant of the Li compound exhibits a strong peak, while there is no dielectric anomaly for the Na compound. There seems to be a slight difference in the magnetic ordering that results in a cancellation of the dielectric anomaly for the Na material. In contrast to typical multiferroic materials, such as $TbMnO_3$ or $MnWO_4$, dielectric anomalies in $LiCuFe_2(VO_4)_3$ occur at both magnetic transitions, and in particular, the dominant peak is associated with the higher transition, while in the standard multiferroic materials only the lower magnetic phase is multiferroic [6,7]. This suggests a different magnetoelectric coupling. Recent work from X. Chen *et al.* reported the appearance of a ferroelectric polarization only in the intermediate phase [8].

The main goal of the allocated beamtime was to record neutron powder patterns as a function of temperature to study the crystal structure at several temperatures in the range of 1.5K-300K. The experiment was split into two beamtimes, respectively at the high-intensity D1B diffractometer and the high-resolution D2B diffractometer. During the D1B experiment, we concentrated on the temperature range around the reported magnetic transitions. The second experiment at D2B was carried out to obtain high-resolution powder patterns to investigate structural alterations as a function of temperature. As both experiments were scheduled for September 2020 and February 2021 respectively, the corona pandemic hindered the on-site presence of our experimental team. Hence, the full on-site control of the experiment was carried out by our local contact Thomas Hansen. The experimental course was supervised remotely from Cologne via mail and phone calls.

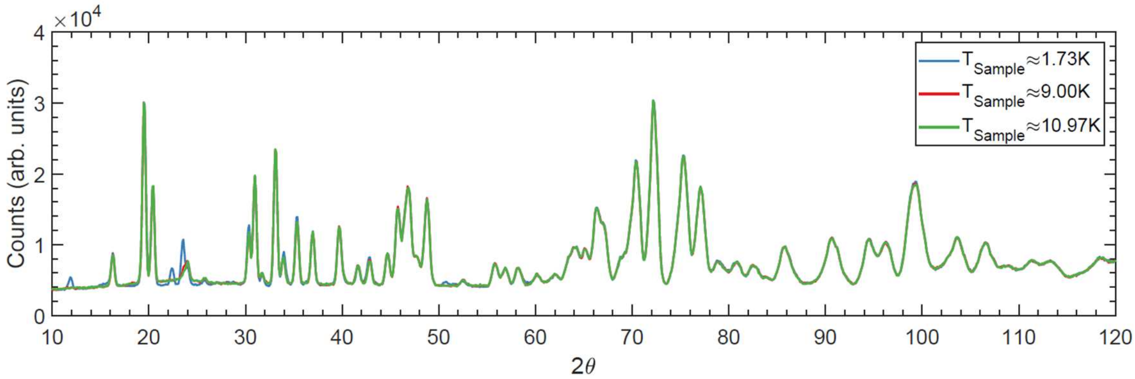

Figure 1: Neutron powder patterns for the Li compound at different temperatures.

As already noted, the first part of the experimental course was about recording neutron powder patterns with small temperature steps across the magnetic transitions for both, the Li and Na compound. Figure 1 displays exemplary powder patterns for the Li system in both magnetic as well as in the paramagnetic phase. From the patterns, shown in Fig 1 it is obvious that additional magnetic reflections develop in the low-temperature phase. In contrast, the presence of additional magnetic signals in the intermediate phase is not clear. Only a developing shoulder of the nuclear reflection at ≈ 24° indicates the presence of a magnetic signal in the intermediate phase. This becomes more obvious when mapping the recorded intensity as a function of scattering angle and temperature. Figure 2 displays a zoom of this mapping around the above-discussed scattering angle. The mapping confirms the appearance of two magnetic reflections below the reported second transition and it also shows some diffuse magnetic signal in the intermediate phase between the nuclear reflection at 24° and the magnetic one at 23.5°.

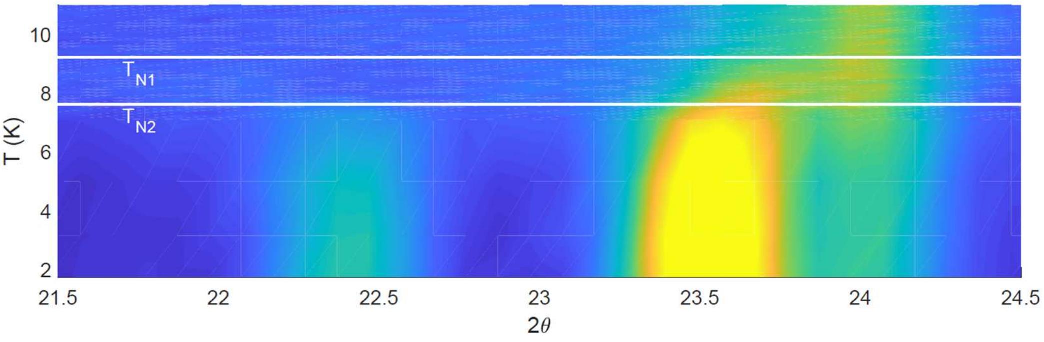

Figure 2: Mapping of the measured intensity around the observed magnetic signals as a function of temperature and scattering angle.

The observation of magnetic contributions to the scattering signal for the Na compound is in contrast not so obvious as it can be seen in the patterns that are exemplarily visualized in Figure 3. Passing the first reported magnetic transition at 9.3K leads only to a small enhancement of intensity at the nuclear reflection at 24°. The right panel of Fig. 3 shows the fitted peak intensity of this reflection, which confirms the onset of additional intensity, which increases below the first transition. However, this signal is very tiny and could be related to the weak Cu moment. No further magnetic contributions are observable in the recorded patterns of the Na system.

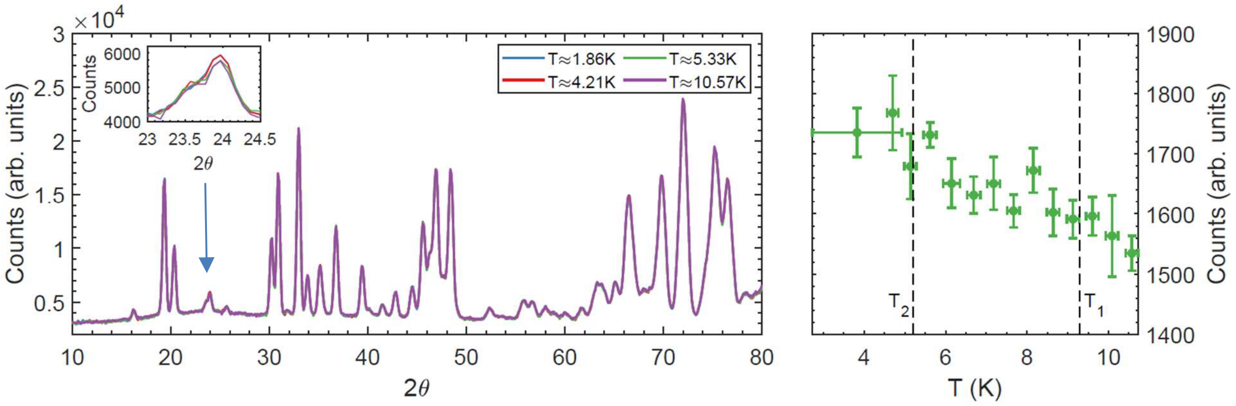

*Figure 3:The left panel shows the recorded patterns for the Na system at different temperatures.*

In the second part of the experimental course, high-resolution patterns were recorded at D2B as a function of temperature. Figure 4. displays exemplary the recorded patterns of the Li compound. The room-temperature pattern differs from the ones below 150K and in particular the appearance of an additional (superstructure) reflection at 20° indicates a structural alteration of the Li system as a function of temperature. A similar outcome was not observable for the Na analogue. For the latter system, the room-temperature pattern resembled the peak intensities and peak positions at low temperature, wherefore no structural transition is expected in this system.

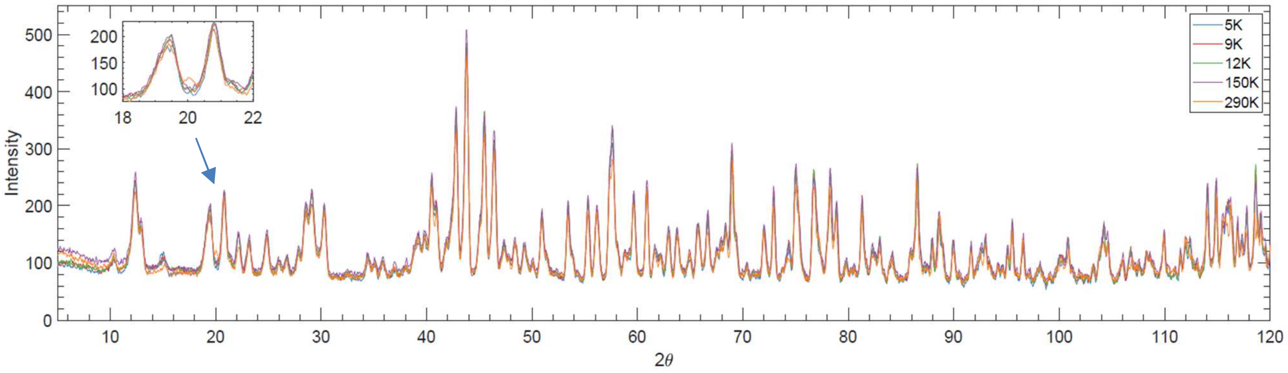

*Figure 4: High-resolution patterns for the Li compound at different temperatures.*

We would like to acknowledge the allocation of this beamtime and especially we would like to thank Thomas Hansen for the excellent on-site support. Despite the challenging pandemic situation and the remote supervision of the experiment, the data collection was highly successful, and the respective analysis will help to characterize the magnetic structure, respectively to understand the multiferroic mechanism that drives the unusual multiferroic behavior in $LiCuFe_2(VO_4)_3$.

[1] J. M. Hughes *et al.*, Am. Mineral. 73, 181 (1988), [2] A. Belik *et al.*, Mater. Res. Bull. 34, 1973 (1999), T. V. Drokina *et al.*, Phys. Solid State 58 1981 (2016), [4] Koshelev *et al.*, Phys. Rev. Applied 10, 034008 (2018) [5] Koshelev *et al.*, arXiv1711.06990 [6] M. Fiebig, J. Phys. D. Appl. Phys. 38 R123 (2005) [7] N. A. Spaldin and R. Ramesh, Nature Materials 18, 203 (2019) [8] X. Chen *et al.*, Inorg. Chem., 61, 2, 944–949 (2022)