ESRF	**Experiment title:** Low-temperature structural study of quantum magnets Li_2CuZrO_4 and Li_2CuHfO_4	**Experiment number**: HE3730
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Shifts: 9	**Local contact(s)**: Adrian Hill	*Received at ESRF:*

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Report:

The goal of our experiment was to study low-temperature structural changes in quasi-one-dimensional (1D) quantum magnets Li_2CuZrO_4 and Li_2CuHfO_4. At room temperature, both compounds feature orthorhombic crystal structures with the *Cccm* symmetry [1]. This symmetry implies that one of the Li positions (Li1) is split. ^{7}Li NMR experiments confirm the disorder of Li atoms at room temperature [2].

Below 100 K, ^{7}Li NMR indicates the slowing down of Li dynamics and the eventual freezing of Li positions. The resulting arrangement of Li atoms should be at least partially ordered, because electron spin resonance (ESR) experiments evidence the formation of two Cu positions that result from the freezing of Li disorder [2]. We attempted to observe this order with low-temperature powder XRD experiments at ID31. Unfortunately, our efforts were futile, and no clear signatures of low-temperature structural changes could be detected. Figure 1 shows experimental powder patterns of Li_2CuHfO_4 at 10 K along with the peak positions expected from the fully relaxed crystal structure with ordered Li atoms (*Pnnm* symmetry). No reflections violating the C-centering were observed.

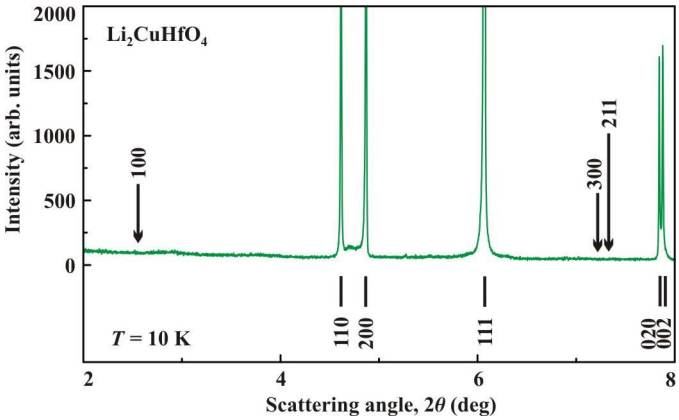

Figure 1. Low-temperature high-resolution XRD powder pattern of Li_2CuHfO_4. Ticks denote the reflections compatible with the Cccm space group, whereas arrows mark the reflections anticipated in the low-temperature *Pnnm* phase.

While low-temperature XRD patterns do not evidence any change in the crystallographic symmetry, temperature evolution of lattice parameters reveals peculiarities of thermal expansion (Figure 2). The thermal expansion along the *b* and *c* directions is weak below 100 K and becomes more pronounced at higher temperatures. By contrast, the *a* lattice parameter remains temperature-independent up to T^* ~ 70 K, shows a very weak increase up to 200 K, and changes to a normal linear expansion at higher temperatures, only. Since the Li1 position is split along the *a* direction, we speculate that the unusual trend observed for the *a* lattice parameter is a signature of Li freezing. Unfortunately, this observation does not give us any detailed

information on the nature of the low-temperature structure. Other methods should be used to get further insight into the precise low-temperature arrangement of Li and Cu atoms.

We have also explored the crystal structure of Li_2CuHfO_4 at high temperatures. At room temperature, Li_2CuHfO_4 is pseudo-tetragonal, with b = 5.8604 Å and c = 5.8334 Å. The difference between the b and c parameters decreases upon heating. Eventually, Li_2CuHfO_4 becomes tetragonal at 650 K (compare to 1320 K for Li_2CuZrO_4 [1]). The transition is of the second order, according to the continuous evolution of the cell volume (not shown). The high-temperature structure is similar to that of β-Li_2CuZrO_4 [1].

Altogether, our high-resolution XRD experiment provides new insight into structural peculiarities of Li_2CuHfO_4. In the future, we plan to apply other techniques, including Raman spectroscopy and magic-angle-spinning NMR, that are more sensitive to the local structure and may help to elucidate the local order of Li atoms in Li_2CuHfO_4 and Li_2CuZrO_4.

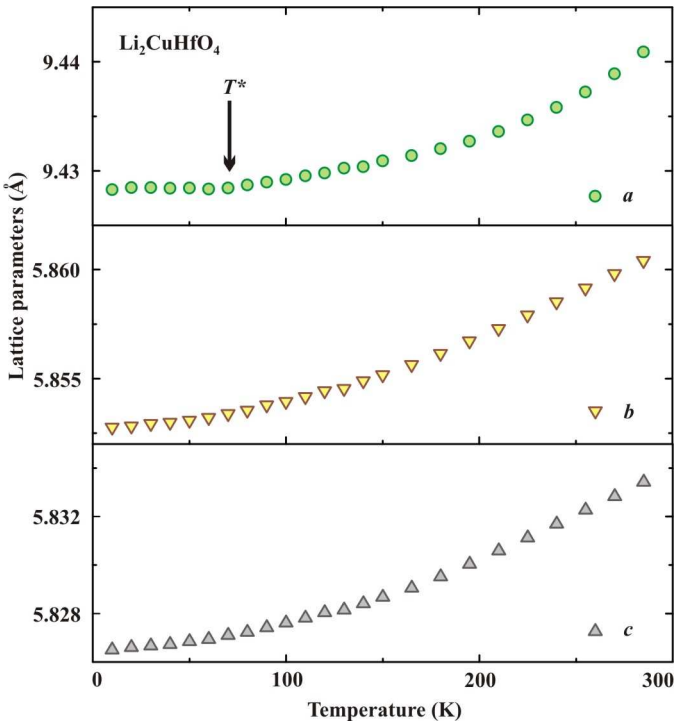

Fig. 2. Thermal expansion of Li_2CuHfO_4. Note the peculiar evolution of the a parameters around T^* ~ 70 K

References:

[1] C. Dussarrat *et al*. J. Solid State Chem. **166**, 311 (2009).

[2] E. Vavilova *et al*. Europhys. Lett. **88**, 27001 (2009).