ESRF **Beamline:** ID22 **Shifts:** 9	**Experiment title:** Crystal structures of relativistic lacunar spinels $GaTM_4Se_8$ (TM = Nb, Ta) **Date of experiment:** from 18.02.2022 to 21.02.2022 **Local contact(s):** Andrew Fitch	**Experiment number:** HC-4580 **Date of report:** 12.08.2022
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In this experiment, we sought to resolve low-temperature crystal structures of relativistic lacunar spinels $GaTM_4Se_8$. These compounds feature TM_4 tetrahedra with an electronic degeneracy that triggers a Jahn-Teller distortion on cooling. An exact manifestation of this distortion depends on the relativistic effect of spin-orbit coupling that occurs in heavy elements such as Nb and Ta.

The experiment was very successful, as we were able to pinpoint phase transitions in both compounds and resolve low-temperature crystal structures for the first time. Here, we present the results obtained for $GaTa_4Se_8$, whereas the behavior of $GaNb_4Se_8$ is generally similar. At room temperature, $GaTa_4Se_8$ features the face-centered cubic crystal structure of a lacunar spinel ($F\bar{4}3m$). On cooling, peak splitting was observed at 44 K. Whereas the 400 cubic reflection splits into three, the 444 reflection is not split (Fig. 1). This is indicative of an orthorhombic distortion. Aided by the single-crystal XRD data collected in the lab on the same compound, we identified the metrics of the low-temperature structure as $a \times a \times 2a$ and refined the model with the $P2_12_12_1$ symmetry. This symmetry is non-polar. However, deformations introduce polarity into individual Ta_4 tetrahedra, so overall we observe an antiferroelectric transition, which is consistent with the dielectric measurements reported recently on this compound [1]. It is worth noting that the ultra-high resolution available at ID22 was essential to resolve the orthorhombic distortion. Previously, the low-temperature phase of $GaTa_4Se_8$ was thought to be tetragonal [2], and the recent preprint [3] repeats this wrong claim, because neutron data with the much lower resolution have been used for the structure analysis.

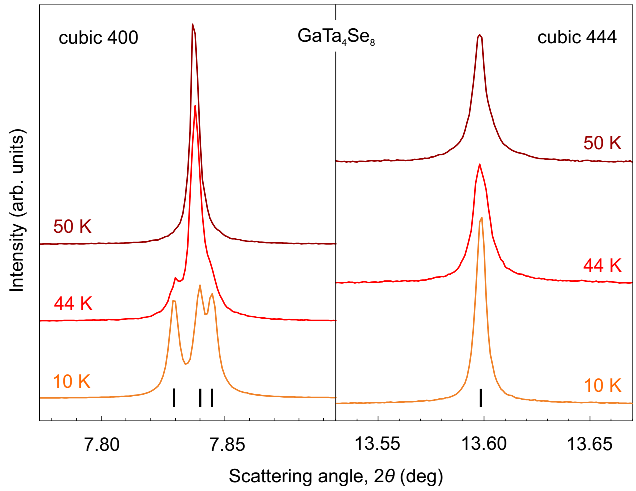

Figure 1: Temperature evolution of the 400 and 444 cubic reflections. Note the coexistence of the cubic and orthorhombic phases at 44 K.

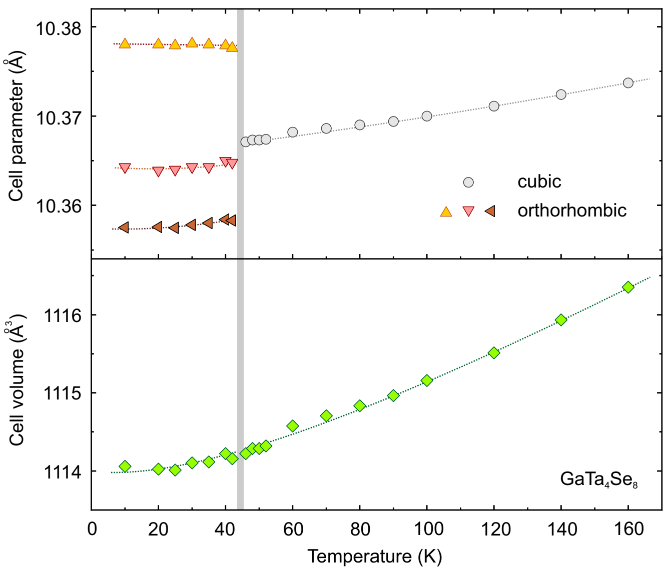

Figure 2: Temperature evolution of the lattice parameters and unit-cell volume for $GaTa_4Se_8$.

Some further remarks are in order:

1) We observe the transition at 44 K, whereas thermodynamic measurements return the transition temperature of 52 K [1]. This mismatch may be due to beam heating, although we checked that attenuation of the beam with second "basler" camera did not increase the transition temperature (one camera was introduced into the beam in all measurements because temperatures below $40 - 50$ K could not be reached otherwise). Therefore, it is possible that some temperature gradient between the capillary and thermometer is present in the custom ID22 cryostat.

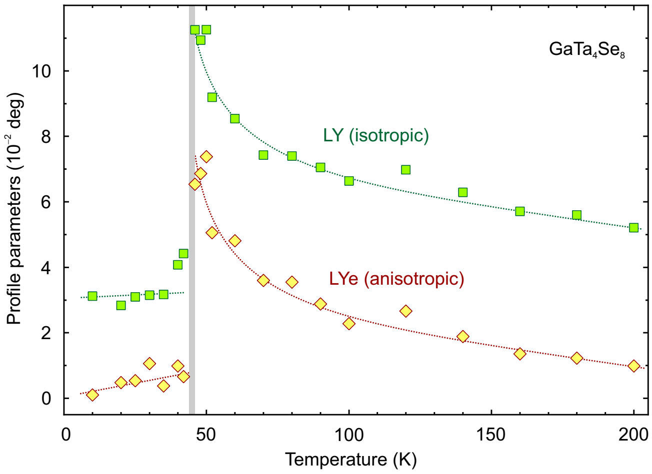

Figure 3: Temperature dependence of the isotropic (LY) and anisotropic (LYe) profile parameters. The definition of LY and LYe is according to Jana2006.

2) Although unit-cell volume shows no discontinuity at the transition (Fig. 2), there is a clear coexistence of cubic and orthorhombic phases at 44 K. Therefore, the transition is first-order.

3) A rather peculiar temperature dependence of the profile parameters is observed. On approaching the phase transition, peaks of the cubic phase progressively broaden and then become much more narrow in the low-temperature phase. This broadening suggests strong precursor effects in the cubic phase of $GaTa_4Se_8$.

We are now completing this study with an *ab initio* calculation of the local electric polarization and plan to prepare the publication shortly.

References:

[1] M. Winkler *et al.* arXiv:2206.15200.

[2] H. Ishikawa *et al.* Phys. Rev. Lett. **124**, 227202 (2020).

[3] T.-H. Yang *et al.* arXiv:2206.07738.