Experimental report

25/01/2024

Proposal: 5-15-635 **Council:** 4/2023

Title: Elucidating the incommensurate structure of the K2PbCu(NO2)6 elpasolite

Research area: Chemistry

This proposal is a new proposal

Main proposer: Matthew CLIFFE

Experimental team: Madeleine GEERS
Matthew CLIFFE
AMELIA THOMPSON
Simarun PRASAD

Local contacts: Laura CANADILLAS DELGADO
Oscar Ramon FABELO ROSA

Samples: K2 Cu Pb N6 O12

Instrument	Requested days	Allocated days	From	To
D19	9	9	08/11/2023	17/11/2023
D9	4	4	02/12/2023	06/12/2023

Abstract:

K2PbCu(NO2)6 compound exhibits several phase transitions involving commensurate and incommensurate structures. This is a unique example where the Jahn-Teller effect gives rise to modulated structural distortions promoting the phase transitions. Our aim is to elucidate the frustration mechanism that trigger this phase transition. For this purpose we kindly requested beam time on the D19 single crystal diffractometer, to collect three full acquisitions at RT (phase I), 275 K (phase II) and 250 K (phase III). Moreover, we will follow the evolution of the incommensurate wave vector as function of T, measuring three short scans in steps of 5 K during the cooling down. We will use the 4-circle displex on D19 operated at 1.45 Å in order to separate properly the satellites from the main reflections. We estimate that at least 3 days for each temperature is necessary, (total of 9 days) on D19 for the complete structural studies and the temperature evolution of the incommensurate wave vector.

Report of experiment 5-15-635.

Elucidating the incommensurate structure of the $K_2PbCu(NO_2)_6$ elpasolite compound.

The experiment was conducted on instrument D19 on 8th November 2023.

The sample was wrapped in aluminium foil, to avoid direct contact with the glue, and mounted on a 1mm diameter vanadium sample holder. Three measurements were carried out at room temperature, 276 K and 250 K with a wavelength of 1.45 Å. The unit cell was also measured as a function of temperature and the temperature range in which the incommensurate structure appears was delimited between 279K and 273K. The measurements consisted of several ω scans at different values of φ and χ to cover the corresponding limit sphere according to the crystalline system. The images were processed with the D19-specific retreat and d19abscan software.

The data measured at room temperature allowed us to solve the crystal structure, proving that there are differences with the model described in previous papers. The position of the Pb atoms in our structure corresponds to Wyckoff position *4a* while Cu is positioned at *4b*, contrary to the proposed model.

For simplicity in data processing, the collection at 276 K was indexed with a conventional cell type I instead of the one proposed in the literature as type F. The type I cell found corresponds to 7.5984 10.55 7.6062 90 90 90 and q = 0.4 ***c****. The data processing is still in progress, although we have already been able to obtain a first model where the modulation of the distances in the Cu environment, due to the Jahn-Teller effect, can be appreciated (see figure 1).

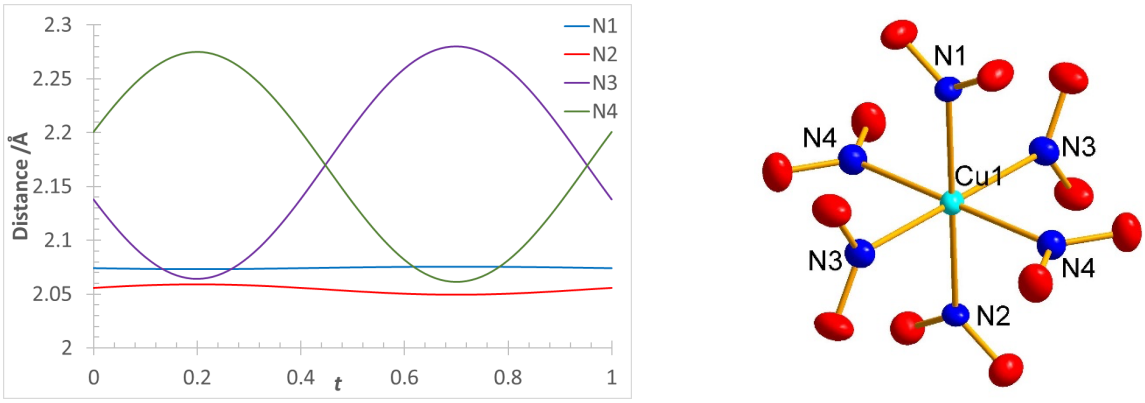

Figure 1. **Left.** Representation of the Cu-N distance in function of the incommensurate *t* parameter obtained from D19 data collected at 276 K. **Right.** Detail of the average Cu environment at 276 K.

At lower temperatures, the measurement at 1.45 Å was not sufficient to determine the structure unequivocally. The increase in the asymmetric unit below 273 K increases the number of parameters to be refined so that it was not possible to obtain enough unique reflections with the wavelength used. It is therefore planned to request a continuation and thus complete the measured data.