Experimental report

27/08/2022

Proposal: 5-41-1143 **Council:** 4/2021

Title: Magnetic phase diagram investigation of the organic geometrically frustrated compound TNN¿CH3CN (LT-Part)

Research area: Physics

This proposal is a new proposal

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Samples: C39H48N7O6C2H3N

Instrument	Requested days	Allocated days	From	To
D10	7	7	29/09/2021	06/10/2021

Abstract:

The S = 1/2 geometrically frustrated spin systems cases are fascinating due to the interplay between quantum fluctuations and geometric frustration, which is less understood. We have succeeded in synthesizing the new triangular compounds TNN.CH3CN which has a unique two-dimensional structure.
Our recent study by means of macroscopic measurements at low temperature and in high magnetic fields revealed that two antiferromagnetically ordered phases exist: One is below 0.25 K at fields below 1.24 T and another is below 0.34 K between 8.45 T and 11.28 T. Above 11.28 T, magnetization reaches full saturation. In the field range 1.24-8.45 T, where the magnetization takes a constant value at 1/3 of full saturation moment no long-range order was observed down to 10 mK.
In this proposal we apply for 7 days of beam time on the diffractometer D10, working first with the special Eulerian cradle and dilution insert to collect structural diffraction data in the paramagnetic phase (T ~2K), then to collect data in the magnetically ordered phase (T < 0.25K). These data will allow us to refine the nuclear structure at low temperature and to determine the magnetic structure of the phase

Report of experiment 5-41-1143:

Title: Magnetic phase diagram investigation of the organic geometrically frustrated compound TNN·CH3CN (LT-Part)

This experiment was performed in ILL (Grenoble, France) at D10 from 29/09/21 to 06/10/21 (7 days). Several measurements were performed on one single crystal of TNN·CH3CN with λ = 2.36 Å. This crystal was previously measured at RT in D19 (second crystal) to check the quality of the nuclear reflections.

The crystal was kept inside the quartz and aluminum holder with a drop of CH3CN (acetonitrile) until the experiment started. Then it was glued to a pin with STYCAST black.

RT:

First the sample was centered at RT. As the orientation of the crystal was unknown, some φ-scans of about 90º width were taken for several values of χ. Finally, the crystal was orientated using the (0 0 -6) reflection.

However, once the dilution refrigerator was installed, we had to orientate again the crystal, since it was placed in a different position. Several φ-scans were taken again using the (0 0 -6) and (1 1 3) reflections.

After some technical problems (one of the dilution arms collided with the optical nose), we had enough reflections to try to determine the UB matrix. Nevertheless, both the (1 1 3) and (2 0 2) and the (0 0 6) and (0 2 4) reflections appear very close to each other in 2θ. Therefore, we cannot decide for now between two possible indexations:

Cooling:

While the sample was cooling from RT to 0.1 K, some φ-scans of strong reflections allowed us to determine that the indexation 2 is the correct one.

Using the Rplot software and the UB matrix for indexation 2 we obtained the list of hkl for the space groups R3c and P1. The goal was that if a reflection only contained in the P1 list appeared, then we would know that the propagation vector is (0,0,0).

0.1 K:

Once the sample reached 0.1 K, we performed mes-scans (ω-scan of about 8º width) of several strong reflections to refine the UB matrix.

Once the UB matrix was refined, we performed several Q-scans and mes-scans to try to observe the propagation vector of the long-range ordered magnetic structure. The scanned directions were:

- Q-scan along h -h -2: (-1 1 -2) → (2 -2 -2)

- Q-scan along 0 -1 l: (0 -1 -3) → (0 -1 -1)
- Q-scan along h -1 -2: (-1 -1 -2) → (1 -1 -2)
- Mes-scan of reflections belonging to P1, 70 reflections measured.
- Q-scan along h -h -2: (-1 1 -2) → (2 -2 -2)
- Q-scan along 0 -1 l: (0 -1 -3) → (0 -1 -1)
- Q-scan along h -1 -2: (-1 -1 -2) → (1 -1 -2)

From all the measurements performed until this point, reflections with intensity were observed only at allowed hkl by the space group R3c, implying no magnetic order seen.

Since the expected magnetic signal is very small and we were observing a relatively high background, we installed the analyzer (smaller detector with a monochromator so that only elastic scattering is detected. Much fewer counts but also almost no background noise).

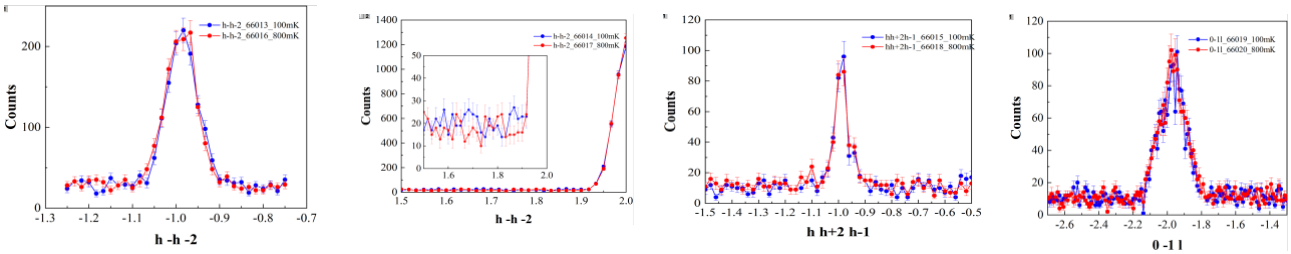
First the new detector was centered using the reflection (2 -2 4).

0.1 vs 0.8 K:

Then, several mes-scans were measured below (0.1 K) and above (0.8 K) the transition temperature for the (1 0 1), (1 1 0), (0 -1 -2), (0 2 1) and (0 -1 -5) reflections. However, no appreciable change was observed in the intensity of the reflections:

Finally, several measurements were performed with much more statistic (3 to 7 times more) below and above the transition temperature:

- Q-scan along h -h -2: (-1.25 1.25 -2) → (-0.75 0.75 -2)
- Q-scan along h -h -2: (1.5 -1.5 -2) → (2 -2 -2)
- Q-scan along h h+2 h-1: (-1.5 0.5 -2.5) → (-0.5 1.5 -1.5)
- Q-scan along 0 -1 l: (0 -1 -2.7) → (0 -1 -1.3)



- Mes-scan of reflection (1 1 0)
- Mes-scan of reflection (0 -1 -2)

- Q-scan along h h -2: (-1.5 -1.5 -2) → (-0.5 -0.5 -2)

Again, no clear signal could be distinguished as only present at the lowest temperature.

Several factors can play a role in the weakening of the magnetic neutron intensity measured: small value of the spin S = 1/2, magnetic moment delocalized in the nitronyl-nitroxide group, big unit cell (around 5866 Å), difficulty to growth deuterated single crystals, and crystallization and size of crystals is hard to control (small crystals).

Therefore, the neutron diffraction experiments performed on this sample were not able to distinguish if the lack of long-range magnetic order is due to a very weak signal hidden in the background or to an incommensurate magnetic structure with a propagation vector in a different direction not scanned in these measurements.

References:

[1] S. Nakatsuji et al. Spin Disorder on a Triangular Lattice. Science 309, 1697 (2005) https://doi.org/10.1126/science.1114727