Experimental report

27/08/2022

Proposal: 5-41-1119 **Council:** 10/2020

Title: Magnetic phase diagram investigation of the organic geometrically frustrated compound TNN·CH3CN

Research area: Physics

This proposal is a new proposal

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Samples: C39 H48 N7 O6 C2 H3 N

Instrument	Requested days	Allocated days	From	To
D19	5	5	28/09/2021	03/10/2021
D10	7	0		

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 revealed that two 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 single crystal diffractometer D10 and 5 days at D19 to refine the nuclear structure at low temperature and to determine the magnetic structure of phase at zero field.

Report of experiment 5-41-1119:

Title: Magnetic phase diagram investigation of the organic geometrically frustrated compound TNN·CH3CN

Motivation:

Geometrically frustrated spin systems such as triangular-lattice antiferromagnets have been the subject of intensive study both by theory and experimental point of view over the last few decades. When periodic order is suppressed, qualitatively new quantum phases like a spin liquid can emerge. Recently, the S = 1 triangular-lattice antiferromagnet NiGaS4 has been reported to show a disordered spin state [1]. The S = 1/2 cases are more fascinating due to the interplay between quantum fluctuations and geometric frustration, which is less understood.

By rational designing of organic tri-radicals, an equilateral triangle of S = 1/2 spins can be constructed. Since the anisotropy of the g-factor of these nitroxide-based compounds is less than 0.5 %, the electron spins are fully isotropic. These would be the best realizations of fluctuating spin system, which will show novel collective phenomena.

We have succeeded in synthesizing the new triangular compounds TNN·CH3CN, (TNN = 1,3,5-Tris(nitronyl nitroxide)benzene) which has a distorted Kagomé lattice structure. The compound TNN·CH3CN has a unique two-dimensional structure, i. e., a regular triangular lattice with two sub-lattices of corner-sharing equilateral triangles: one formed by intramolecular exchange couplings and the other by intermolecular ones. The two-dimensional sheet is spread within the ab-plane by the contact between the nitroxide groups. The intermolecular contact along the c-axis can give inter-sheet interactions. An estimation of the intramolecular antiferromagnetic exchange constant, based on a careful analysis of the magnetization versus magnetic field curves of liquid TNN·CH3CN, gives J_{AF} = -6 K.

The macroscopic measurements (specific-heat, magnetization, magnetic torque and magneto-caloric effect) performed at low temperature and in high magnetic fields revealed that two antiferromagnetically ordered phases exist at very low temperature: 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 (1/3-magnetization plateau), no long-range order was observed down to 10 mK.

In this proposal we plan to collect data at 2K in order to refine the nuclear structure in the paramagnetic phase. At the same time, measurements were performed in the paramagnetic phase (2K) and in the magnetically ordered phase (T < 0.25K) on the single crystal diffractometer D10. These data will allow us to determine the magnetic structure at zero magnetic field. In subsequent proposals we will undertake the exploration of the magnetic phases at low and high magnetic field.

Experiment 5-41-1119:

This experiment was performed in ILL (Grenoble, France) at D19 from 27/09/21 to 01/10/21 (5 days). Several measurements were performed on 5 different single crystals of TNN·CH3CN with λ = 1.45 Å. Before the experiments, only one of the crystals was kept with a drop of solvent (acetonitrile, CH3CN) inside the glass capillary (right image). All of them were kept in a freezer at -20ºC.

First, all the crystals were checked to see how they scattered, since none of them had good quality:

- First crystal: the crystal, of around 1 mm³, was glued to a vanadium pin (1 mm) with X60 Schnellklebstoff. Then the sample was centered at RT. While the vacuum was created inside the cryostat and the temperature was decreased to 20 K, several ω-scans were performed to check the quality of the crystal. However, a signal was seen around $2\theta = 7º$ almost always present, which sometimes seemed like a double peak. Another signal was also seen for slightly higher 2θ around $\omega = 47º$, also a bit elongated. This could indicate that is a crystal with twins. To be safer we decided to change the sample and check if the other crystals scatter better.
- Second crystal: the crystal was put inside a quartz holder with an aluminum tap. Inside the holder we put one drop of CH3CN (acetonitrile). The sample was glued inside the holder at 14 mm from the top with the help of vacuum grease. Then the sample was centered at RT. A quick ω-scan revealed the same kind of signal around $2\theta = 7º$ at all values of ω, so we decided to check the next crystal.
- Third crystal: the crystal was prepared in the same way as the second. Then the sample was centered at RT and several measurements were performed. Again, we observed the signal around $2\theta = 7º$ at almost all values of ω. However, this time the reflections looked more circular, and with the help of the Int3D software the cell parameters could be obtained from the observed reflections.
- Second crystal: to be sure, we checked again this crystal by measuring several ω-scans at RT. After analyzing the data with Int3D, the integrated reflection list of the second crystal looks better than the third one. The reflections observed included the (0 0 -6), (2 0 -4) and (2 -1 -3). We decided to use the second crystal for the D10 experiment and check the rest of the crystals to see if any of the others is better for D19.
- Fourth crystal: similar preparation and results as in the previous crystals. However, some reflections are observed too close to each other.
- Fifth crystal: similar preparation and results as in the previous crystals. However, the signal observed is weaker (the crystal is smaller).

Finally, we decided to measure the third crystal for the rest of the experiment and try to obtain as many reflections as possible at 2 K. The sixth crystal was not checked since the size was even smaller than the fifth one.

For the low temperature the quartz holder with the crystal was inserted inside a compact 3-stage displex. Due to a problem with the quartz holder when the vacuum pump started to work, it was sealed to the aluminum tap with X60 Schnellklebstoff. However, after several ω-scans at RT and 20 K, we decided to finish the experiment, since very few good reflections are observed and more measurements would not provide more information.

References:

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