Experimental report

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Proposal: DIR-206 **Council:** 4/2020

Title: Powder diffraction on a prominent single-ion magnet to gain access tomolecular magnetic anisotropy

Research area: Chemistry

This proposal is a new proposal

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Samples: C58 H58 B Dy F20

Instrument	Requested days	Allocated days	From	To
D20	3	3	06/07/2021	09/07/2021

Abstract:

In this proposal, we suggest using a novel approach for retrieving the magnetic anisotropy of a single-ion magnet (SIM) from a magnetic powder diffraction measurement. Magnetic anisotropy is a quantity at the heart of molecular magnetism, providing important clues about magneto-structural correlations in SIMs, but its experimental recovery is hindered by the fact that only diffraction techniques are generally applicable to all compounds. The step forward from performing the experiment on single-crystals, a technique which is already well-established from experiments at both the LLB (France) and the HFIR (US) is therefore an important one, with the powder approach shown to be possible in a recent benchmark experiment.
We now suggest to perform this powder diffraction experiment on a prominent Dy(III)-based compound that was the first example in a range of compounds that show molecular magnetic hysteresis close to the current record-high temperature of 80 K. The successful completion of the proposed experiment and the promise of obtaining experimental knowledge about magnetic anisotropy from a powder measurement is therefore sure to make a substantial impact in the SIM-community

Powder diffraction on a prominent single-ion magnet to gain access to molecular magnetic anisotropy

Single-molecule magnets (SMMs) are metal-organic complexes that can retain a magnetic moment for a long time after the removal of an external magnetizing field. This purely molecular effect manifests itself in the opening of a hysteresis loop below a characteristic blocking temperature. It was first shown to appear in a Mn_{12}-cluster.[1] The molecular magnetic effect itself originates from significant spin-orbit coupling within the molecule, which gives rise to anisotropic magnetic properties and consequently to an energy barrier to magnetic reversal.

To improve upon the fascinating properties of molecular magnets, it is imperative to understand the nature of the anisotropic magnetic behavior that is intimately correlated with the molecular structure. In particular, the direction of the magnetic easy-axis of the molecule, which is the direction of largest magnetization under an applied field, gives a clear indication of the ligand field effect on the metal ion(s) in a molecule.

The local magnetic anisotropy in paramagnetic compounds can be assessed using polarized neutron diffraction (PND) via the site susceptibility model, a method developed by Gukasov and Brown.[2] The method has been used successfully to experimentally determine the susceptibility tensor of SMMs in several studies.[3-6] Recently, an analogous method using polarized neutron powder diffraction (PNPD) has been developed by Kibalin and Gukasov,[7] alleviating the need for large single-crystals and measurements at multiple magnetic field orientations. However, only a single study have pursued the site susceptibility PNPD method so far.[5]

In this study, two systems were examined:

Crystals of the type $[Co(L_2)_2][(TBA)_2$ **(1)** (TBA: Tetrabutylammonium) (L: N,N'-bis(4-chlorophenyl)oxanilido), synthesized in the group of Franc Meyer – University of Göttingen.

Crystals of the type $[Dy(Cp^{ttt})_2]^{2+}$ **(2)** (Cp^{ttt}: $C_5H_2{}^tBu_3$-1,2,4) synthesized in the group of David Mills – University of Manchester. Unfortunately, the measured data quality of **(2)** was very low, as the crystals had been compromised during delivery, due to their highly air-sensitive nature.

PNPD data was collected at the high-flux powder diffractometer D20 of the Institut Laue-Langevin (ILL) [8] on a powdered sample of **(1)**. Data was measured at 5 K under an applied magnetic field of 1 T, with neutrons with wavelength 2.41 Å. A piece of cadmium was placed in the top of the sample cylinder, in an attempt to prevent preferred orientation, as there have been reports of induced preferred crystallite orientation with the application of large magnetic fields to magnetically anisotropic powder samples.[5,7] The neutron beam was polarized using a ^{3}He spin filter inserted in the beam path.[9] Using software provided by the ILL, the data was corrected for the time-dependent polarization efficiency of the ^{3}He cell.

The magnetic site susceptibility tensor of the Co(II)-ion of **(1)** has been refined using the Python-package Cryspy (version 0.5.9) through Cryspy_editor (version 1.5.7).[7] Together with a crystal structure from single-crystal X-ray diffraction, measured at 20 K at the Spring8 Synchrotron, a fit was obtained with a $\chi^2 = 1.30$ (using the

difference pattern). The fit included offset of the beam (2θ), scale factor, background (a set of points with linear interpolation between them), shape parameters (U, V, W) and finally the susceptibility parameters.

A draft publication has been prepared and publication is expected within the next 3 months.

References

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