High-Field EPR Studies on an Oriented Single Crystal of a Mn(III)-Based Mononuclear Single-Molecule Magnet

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Introduction

Spin relaxation properties of mononuclear transition metal complexes have recently been under thorough investigation. The $[Mn\{(OPPh_2)_2N\}_3]$ complex (**1**), which contains a high spin $S = 2$ Mn(III) center, exhibits field-induced slow relaxation of its magnetization, i.e., properties akin to those of a Single-Molecule Magnet (SMM) [1]. The Mn(III) center is coordinated by three chelating $[(OPPh_2)_2N]^-$ ligands, giving rise to an MnO_6 coordination sphere that is Jahn-Teller (JT) tetragonally distorted (elongated) [1]. The JT elongation leads to a ground state exhibiting a negative zero-field splitting (zfs) parameter, *D*. Previous investigations by SQUID magnetometry and parallel mode X-band EPR spectroscopy [1] provided estimates of the spin Hamiltonian parameters for **1**, which were more recently accurately determined by HFEPR on a powder sample [2]. In the work reported herein, an oriented single crystal of **1** was investigated at magnetic fields up to 35 T, in an effort to determine the orientation of the zfs tensor with respect to the molecular frame of **1**.

Experimental

The DC Facility of the NHMFL was used including a 35-T resistive magnet. Cavity perturbation method was employed in conjunction with an MVNA vector analyzer serving as an EPR spectrometer.

Results and Discussion

An oriented crystal of **1** was placed in a horizontal rotating cavity so that the orientation of magnetic field may be changed in the plane of natural crystal face. By observing the position of the resonance peaks, the crystal was rotated such that one of the magnetic hard axes is aligned parallel to the magnetic field. Multi-frequency EPR spectra were then recorded for this orientation at a temperature of 4.2 K for the frequency range from 45 GHz to 320 GHz. The plot of frequency as a function of resonant field positions is shown in Fig. 1. The fit of the measured EPR peak position with respect to effective spin Hamiltonian is shown as solid lines. The parameters for which a good fit was obtained are as follows: effective spin of $S = 2$, axial anisotropy (D) of -3.92 cm^{-1}, transverse anisotropy (E) of 0.02 cm^{-1}, g of 2.0 and higher order anisotropy of about 0.0036 cm^{-1}. These parameters are consistent with those of the previously reported powder studies [2].

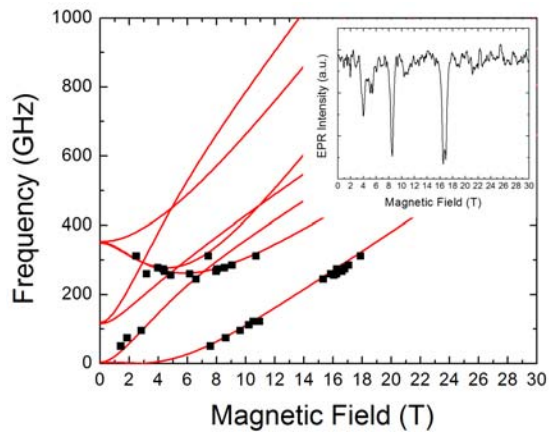

Fig. 1. Plot of EPR frequency as a function of resonant magnetic field. The black solid points represent the measured EPR peaks and the red lines correspond to fit using spin Hamiltonian parameters as in text. Inset shows an exemplary EPR spectrum measured at 277 GHz.

Conclusions

An oriented crystal of a Mn(III)-based mononuclear SMM (**1**) was studied at magnetic fields up to 35 T. Analysis of the data confirmed the spin Hamiltonian parameters obtained by powder HFEPR studies. Based on this work, the orientation of the zfs tensor with respect to the molecular structure of **1** will be determined.

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References

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[2] Grigoropoulos, A., *et al*., NHMFL Research Report #222 (2013).