

Experimental report

03/12/2016

Proposal: 4-06-1

Council: 4/2015

Title: Crystal-field spectroscopy of symmetry-lowered mononuclear dysprosium and erbium single-molecule magnets

Research area: Chemistry

This proposal is a new proposal

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Samples: C₂₄H₄₄LaNO₈Pt₂S₈
C₂₄H₄₄CeNO₈Pt₂S₈
C₂₄H₄₄NO₈PrPt₂S₈
C₂₄H₄₄NNdO₈Pt₂S₈
C₂₄H₄₄NO₈Pt₂S₈Sm
C₂₄H₄₄NO₈Pt₂S₈Tm
C₂₄H₄₄NO₈Pt₂S₈Yb

Instrument	Requested days	Allocated days	From	To
IN4	3	3	30/05/2016	03/06/2016

Abstract:

In this experiment, we intend to study crystal-field excitations in mononuclear dysprosium and erbium Single-Molecule Magnets (SMMs) derived from a series of perfectly tetragonal lanthanide SMMs. In the derived systems intended for the proposed experiment, we have rationally lowered the symmetry of the crystal field around the lanthanide ion. From ac magnetic susceptibility experiments, the symmetry lowering is found to worsen the SMM behaviour for the dysprosium system but improve that of the erbium system. The anisotropy barrier responsible for the SMM behaviour is governed by the crystal-field splitting, and these findings therefore indicate that the symmetry lowering affects this splitting in strikingly different ways for dysprosium and erbium. In order to clarify this, we want to probe the crystal-field splitting of these new low-symmetry systems by means of inelastic neutron scattering. The discrimination between crystal-field excitations and phonons will be based, not only on Q- and T-dependencies of the excitations, but also on comparison with the isostructural diamagnetic yttrium compound.

The study of electronic spin-lattice relaxation in mononuclear lanthanide complexes (known as single-molecule magnets or single-ion magnets) has been a hot topic within the field of molecular magnetism, due to reports on unusually long relaxation times resulting from resonant spin-phonon interactions with high-lying crystal field states [1]. For this reason, the determination of crystal field splittings is key to the understanding and tuning of electronic spin dynamics in such systems. Traditionally, the systems under study have been based on the lanthanides from terbium to erbium, due to their superior magnetic moments. Recently attention has been directed towards the earlier lanthanide like Ce [2] and Nd [3], and the very late lanthanides like Yb [4].

We have previously investigated a new family of lanthanide single-molecule magnets with perfectly tetragonal symmetry, the high symmetry making crystal field spectroscopic studies feasible. The compounds come in high- and low-symmetry versions, the difference being whether the tetragonal symmetry is axial or non-axial. The lower symmetry version can be prepared with all the possible lanthanides, and so far the crystal field splittings for the terbium, dysprosium, holmium, and erbium derivatives have been determined from TOF-INS measurements on IN4C (@ ILL), TOFTOF (@ FRMII) and FOCUS (@ PSI). Due to the growing interest in the lanthanides with smaller moments, and in order to map out the effect of the same crystal field on the full series of lanthanide ions, we undertook the crystal field spectroscopic analysis of the Ce, Pr, Nd, Tm, and Yb derivatives by means of TOF-INS at IN4C.

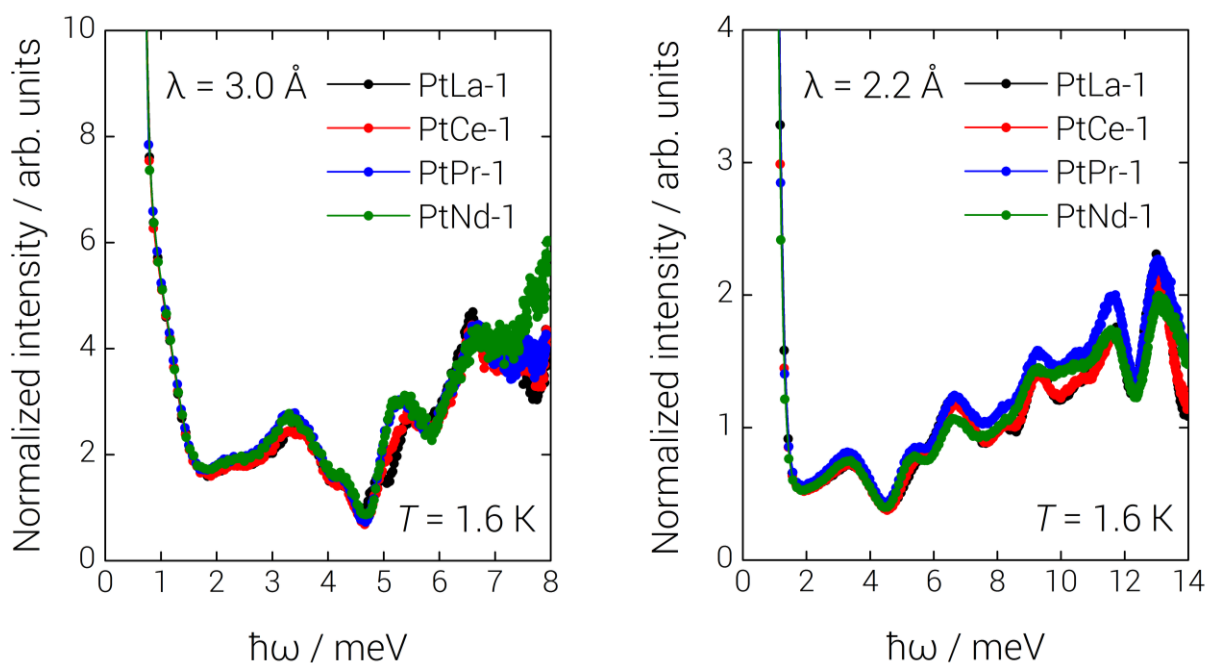


Figure 1. The Q -integrated spectra for the samples PtLa-1, PtCe-1, PtPr-1, and PtNd-1 at $T = 1.6$ K, recorded with $\lambda = 3.0$ Å (left) and $\lambda = 2.2$ Å (right). The data were integrated over the full available Q -range.

The Q -integrated spectra of the samples PtCe-1, PtPr-1, and PtNd-1 at $T = 1.6$ K, recorded with $\lambda = 3.0$ Å and 2.2 Å, are given in Figure 1, together with the analogous spectrum of the isostructural diamagnetic lanthanum complex, PtLa-1. The comparison with the phonon spectrum of the lanthanum complex, suggests the presence of a crystal field excitation at $\hbar\omega \sim 5.2$ meV for the Pr and the Nd complexes. However, the Q - and T -dependencies of the excitations are not supportive of this. Consequently, we assign the excitation to a phonon mode depending on the lanthanide ion. In this way, the substitution of the lanthanide ion causes a frequency shift of the phonon, explaining the gradual change in the relevant part of the spectrum upon going from

lanthanum to neodymium. We were thus unable to observe any crystal field excitations for the early lanthanide derivatives, despite that point charge crystal field calculations on similar systems suggest the presence of INS-allowed excitations in the probed energy transfer window [3].

The Q -integrated spectra of the low symmetry thulium and ytterbium derivatives at $T = 1.6$ K and 50 K recorded with $\lambda = 0.84$ Å and $\lambda = 1.61$ Å, respectively, are given in Figure 2. Crystal field point charge calculations on similar systems suggest the INS allowed $|7/2, \pm 5/2\rangle \rightarrow |7/2, \pm 7/2\rangle$ excitation ($|J, m_J\rangle$ basis, $|7/2, \pm 5/2\rangle$ is the ground Kramers doublet) in PtYb-1 to be at $\hbar\omega \sim 15$ meV [3]. We were however unable to observe a crystal field excitation at this energy transfer. The $|6, \pm 6\rangle \rightarrow |6, \pm 5\rangle$ excitation in PtTm-1 is calculated to be at $\hbar\omega \sim 55$ meV, $|6, \pm 6\rangle$ being the ground pseudo-doublet [5]. Likely as a result of the loss of the relevant Q -region at high energy transfers, and as a result of the background associated with the hydrogen content of the sample, we were also unable to observe this crystal field excitation.

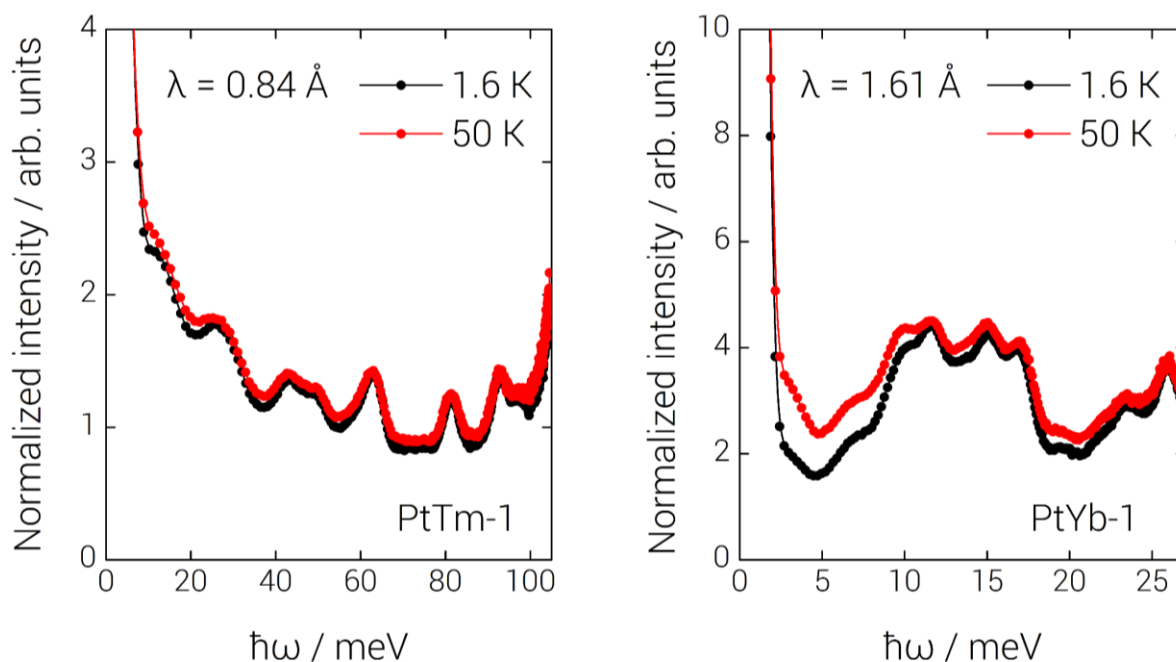


Figure 2. The Q -integrated spectra for the samples PtTm-1 (*left*), and PtYb-1 (*right*) at $T = 1.6$ K and 50 K, recorded with $\lambda = 0.84$ Å and $\lambda = 1.61$ Å, respectively. The data were integrated over the full available Q -range.

[1] S.T. Liddle, J. van Slageren, Chem. Soc. Rev. 44 (2015) 6655–6669. [2] J.J. Le Roy, I. Korobkov, J.E. Kim, E.J. Schelter, M. Murugesu, Dalt. Trans. 43 (2014) 2737–2740. [3] J.J. Baldoví, J.M. Clemente-Juan, E. Coronado, Y. Duan, A. Gaita-Ariño, C. Giménez-Saiz, Inorg. Chem. 53 (2014) 9976–9980. [4] K.S. Pedersen, J. Dreiser, H. Weihe, R. Sibille, H. V. Johannesen, M.A. Sørensen, B.E. Nielsen, M. Sigrist, H. Mutka, S. Rols, J. Bendix, S. Piligkos, Inorg. Chem. 54 (2015) 7600–7606. [5] M.A. AlDamen, S. Cardona-Serra, J.M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, C. Martí-Gastaldo, F. Luis, O. Montero, Inorg. Chem. 48 (2009) 3467–3479.