

# Experimental report

29/10/2015

**Proposal:** 4-04-468

**Council:** 10/2014

**Title:** Crystal-field spectroscopy of tetragonal lanthanide single-ion magnets

**Research area:** Chemistry

**This proposal is a new proposal**

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**Samples:** C24 H44 O8 S8 Pt2 Dy  
C24 H44 O8 S8 Pt2 Er  
C24 H44 O8 S8 Pt2 Y  
C40 H44 O8 S8 Pt2 Dy  
C40 H44 O8 S8 Pt2 Er  
C40 H44 O8 S8 Pt2 Y  
C24 H44 N O8 S8 Pd2 Dy

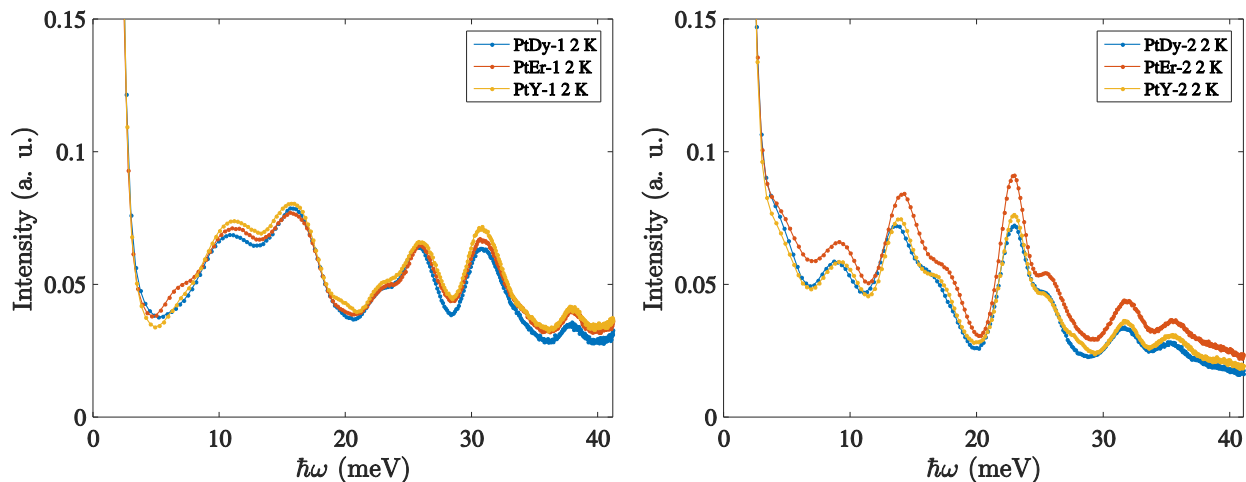
Instrument	Requested days	Allocated days	From	To
IN4	4	4	30/04/2015	05/05/2015

## Abstract:

In this experiment we intend to study crystal-field excitations in perfectly tetragonal dysprosium and erbium single-ion magnets. We have been able to synthesize a system with square antiprismatic geometry, and one where we have twisted the prism around the fourfold axis towards a geometry in-between cubic and square antiprismatic. Using alternating current magnetic susceptibility measurements we have determined that this twist greatly influences the anisotropy barrier of the system. This barrier is governed by the crystal-field splitting, and to gain insight on the processes responsible for the relaxation of the magnetization, we want to probe this splitting by means of inelastic neutron scattering. Through comparison with the isostructural diamagnetic yttrium compounds we will discriminate between phonons and magnetic excitations.

Lanthanide single-ion magnets are mononuclear paramagnetic lanthanide complexes that exhibit slow relaxation of the magnetization in the absence of long-range magnetic order. In a simple picture, the splitting of the ground  $J$  multiplet of the lanthanide ion into its  $m_J$  components, by the surrounding crystal field, generates a barrier for magnetization reversal [1]. However, while such “over-barrier” relaxation via excited crystal field states is often dominating, other relaxation processes can also be relevant, their relevance being intimately linked to the nature of the crystal field splitting of the ground  $J$  multiplet [2]. As a result, ac magnetic susceptibility data have to be complemented by crystal field spectroscopic data in order to understand and assess the spin relaxation processes in such lanthanide single-ion magnets.

In order to facilitate a detailed study of how minuscule structural modifications affect the crystal field splitting and therefore the operative spin relaxation processes, we prepared a novel family of lanthanide single-ion magnets where the lanthanide ion is sandwiched between two squares of oxygen donor atoms in a perfectly tetragonal environment. The twist of the two  $O_4$  squares with respect to each other around the four-fold axis can be varied and in the present study, we investigated the crystal-field excitations in the dysprosium and erbium systems with  $\varphi \approx 23^\circ$  (abbreviated PtDy-1 and PtEr-1), and  $\varphi \approx 45^\circ$  (abbreviated PtDy-2 and PtEr-2). In the PtLn-1 compounds the intermediate twist angle results in exact  $C_4$  point group symmetry at the lanthanide site, while the angle of  $\varphi \approx 45^\circ$  in the PtLn-2 systems results in the higher point group symmetry  $D_{4d}$ . This very high symmetry of the PtLn-2 systems simplifies the parameterization of the crystal field. The studied systems were chosen, as they all exhibit slow relaxation on the magnetization as determined from ac magnetic susceptibility experiments. Furthermore we investigated the isostructural diamagnetic yttrium complexes (abbreviated PtY-1 and PtY-2), thereby facilitating an easy discrimination between magnetic excitations and phonons in the paramagnetic systems. Prior to the IN4 experiment, studies at lower energy transfers were carried out at the cold neutron time-of-flight spectrometer TOFTOF at FRM II, Munich, DE.

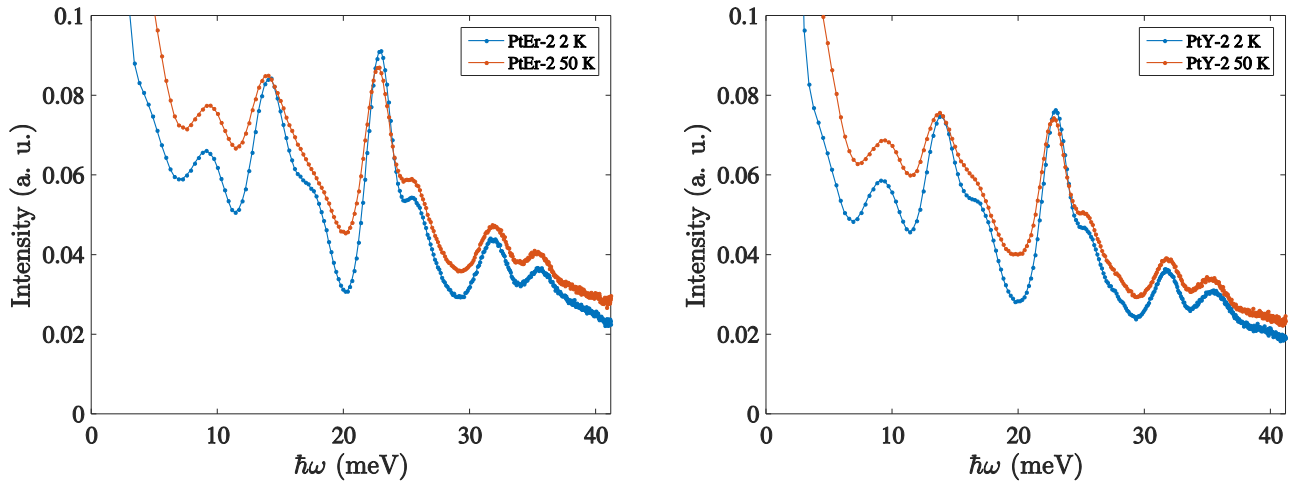


**Figure 1. Left:** INS spectra for PtLn-1 (Ln = Dy, Er, Y) at  $T = 2$  K obtained with  $\lambda_i = 1.3$  Å. **Right:** INS spectra for PtLn-2 (Ln = Dy, Er, Y) at  $T = 2$  K obtained with  $\lambda_i = 1.3$  Å. The data are integrated over the full available  $Q$  range.

The data taken with  $\lambda_i = 1.3$  Å at  $T = 2$  K are shown for the six compounds PtLn-1 (Ln = Dy, Er, Y) and PtLn-2 (Ln = Dy, Er, Y) in Figure 1. For the PtLn-1 systems, the spectra are largely similar in the given energy transfer window (Figure 1 Left). At  $\hbar\omega = 6.6$  meV, a shoulder on the low-energy side of the first phonon mode is observed for PtEr-1, which based on  $Q$  dependence (not shown) and the comparison with the phonon spectrum of PtY-1 (Figure 1 Left, yellow trace) is identified as a magnetic excitation. This is in accordance with the data taken on TOFTOF. For the PtLn-2 systems, the spectra are also largely similar (Figure 1 Right).

However, the PtEr-2 spectrum seems to have a generally increased intensity. The pronounced additionally intensity of the PtEr-2 spectrum in the “valley” between the elastic line and first phonon mode, is the result of the presence of magnetic excitation at  $\hbar\omega = 6.8$  meV, as confirmed by a close inspection of the  $S(Q, \omega)$  map (not shown). This, as well, is in accordance with the data taken at TOFTOF.

An investigation of the temperature dependence of the spectrum of PtEr-2 (Figure 2 Left) seems to suggest that the mode at  $\hbar\omega = 22$  meV could be a magnetic excitation on top of a phonon. However, the loss of the low  $Q$  region of the spectrum impedes a conclusion on the matter. An investigation of the phonon spectrum of the diamagnetic isostructural PtY-2 sample (Figure 2 Right) surprisingly reveals that the phonon mode at  $\hbar\omega = 22$  meV loses intensity upon heating, therefore disproving a partly magnetic origin of the excitation in the PtEr-2 spectrum. This phonon anomaly is yet to be understood, but is also clearly observed when studying the temperature dependence of the PtDy-2 spectrum (not shown).



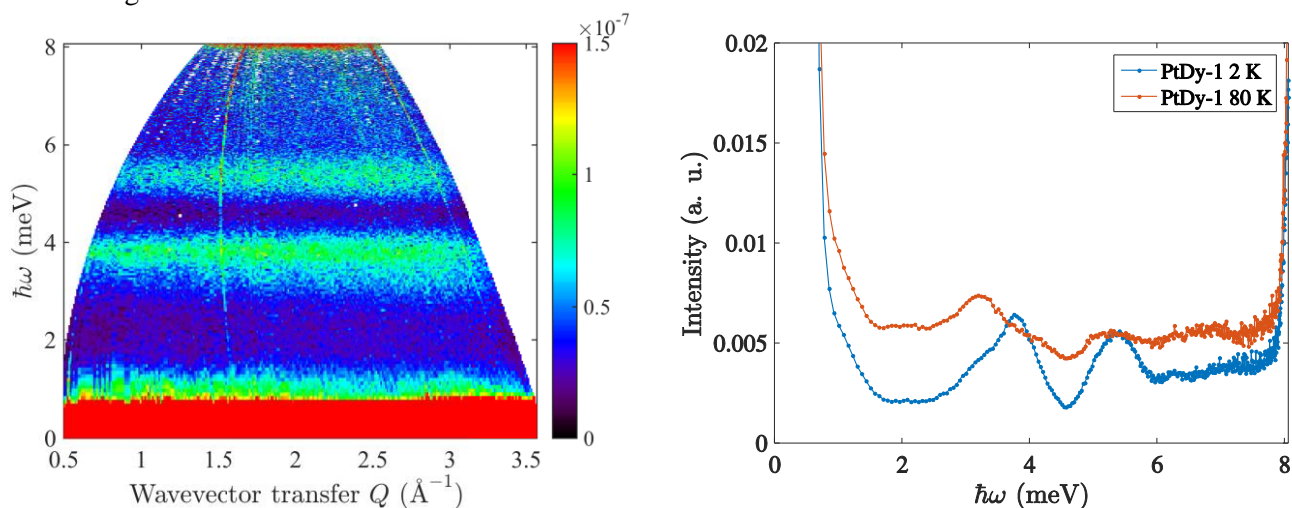
**Figure 2.** INS spectra for PtEr-2 (**Left**) and PtY-2 (**Right**) at  $T = 2$  and 50 K obtained with  $\lambda_i = 1.3$  Å. The data are integrated over the full available  $Q$  range.

In total, no more than one crystal field excitation could be observed for the two erbium systems ( $\hbar\omega = 6.6$  meV for PtEr-1 and  $\hbar\omega = 6.8$  meV for PtEr-2) up to energy transfers of 100 meV. Unfortunately, one spectroscopic observation is too little information to unambiguously determine the electronic structure even when accompanied by bulk magnetic data. However, due to the high symmetry of the crystal field in PtEr-2 the relevant selection rule ( $\Delta m_J = \pm 1$ ) is expected to be strictly obeyed, and consequently a single crystal field excitation should be allowed if the ground state is the one characterized by either the minimum or the maximum value of  $m_J$ . Based on established magneto-structural correlations [3] the latter possibility is by far the most probable, and consequently, based on the INS data, we can with some certainty assign the ground state in PtEr-2 to  $|\pm 15/2\rangle$  ( $|m_J\rangle$  states of the ground  $J$  multiplet), and consequently identify the crystal field excitation at  $\hbar\omega = 6.8$  meV as the  $|\pm 15/2\rangle \rightarrow |\pm 13/2\rangle$  transition. The fact that this picture seems to be largely preserved for PtEr-1 suggests that the admixing of wavefunctions following the symmetry lowering on going from PtEr-2 to PtEr-1 is less pronounced than expected (see below for the discussion for the dysprosium compounds).

For both the dysprosium systems, two low-lying excitations were observed in the TOFTOF experiment, at approximately  $\hbar\omega = 4$  and 5.5 meV, the energy of the two crystal field excitations only differing slightly between the two compounds. For the high symmetry PtDy-2 compound, these two excitations along with bulk magnetic data were sufficient to determine the electronic structure. The crystal field excitations correspond to the  $|\pm 11/2\rangle \rightarrow |\pm 9/2\rangle$  and the  $|\pm 11/2\rangle \rightarrow |\pm 13/2\rangle$  transitions. Due to the high symmetry of the crystal field in the PtLn-2 systems, no more than these two excitations are allowed (selection rule  $\Delta m_J = \pm 1$ ). In support of this,

we observed no crystal field excitations at higher energy transfers up to approximately 100 meV on IN4, as discussed above.

The lowering in point group symmetry on going from the PtDy-2 to the PtDy-1 system is expected to result in an admixture of the wavefunctions, causing a relaxation of the above selection rule. Despite this, we failed to observe any crystal field excitations for PtDy-1 at larger energy transfers up to around 100 meV seen from the IN4 data taken with  $\lambda_i = 1.3 \text{ \AA}$  (Figure 1 Left) and with  $\lambda_i = 0.84 \text{ \AA}$  (not shown). While this can be rooted in the loss of the low  $Q$  part of the spectrum at larger energy transfers, it could also indicate that the admixing of wavefunctions described by different values of  $m_J$  is less pronounced than expected from theory [4]. In order to address this question further we measured INS spectra of PtDy-2 with  $\lambda_i = 3.0 \text{ \AA}$  at  $T = 2$  and 80 K (Figure 3 Right). Provided a sufficient admixing of the states the  $\sim|\pm 9/2\rangle \rightarrow \sim|\pm 13/2\rangle$  hot excitation could possibly be observed. However, this excitation expected at 1.6 meV is clearly not observed in the INS spectrum at 80 K. The temperature of 80 K was chosen in order to populate the  $\sim|\pm 9/2\rangle$  state at 45 K significantly. The  $S(Q, \omega)$  map for PtDy-2 shows the two observed ground state excitations at  $\hbar\omega = 3.9$  and 5.5 meV (Figure 3 Left), confirming the results from TOFTOF.



**Figure 3. Left:**  $S(Q, \omega)$  plot for PtDy-1  $T = 2$  K obtained with  $\lambda_i = 3.0 \text{ \AA}$ . **Right:** INS spectra for PtDy-1 (Ln at  $T = 2$  and 80 K obtained with  $\lambda_i = 3.0 \text{ \AA}$ . The data are integrated over the full available  $Q$  range.

Based on the results obtained on IN4 combined the results already obtained at TOFTOF, we are able to fully or partly deduce the structure of the crystal field split ground  $J$  multiplet in the studied compounds. The data indicate that the effect of the change in the twist angle from  $\varphi \approx 45^\circ$  (PtLn-2) to  $\varphi \approx 23^\circ$  (PtLn-1) can be observed in terms of a slight modification in the energy of the crystal field excitations. However, the ensuing admixture of the states characterized by different values of  $m_J$  is too small for a relaxation of the relevant selection rule, and consequently no additional crystal field excitations could be observed. Finally, the obtained information on the electronic structure of the studied systems, have allowed us to assess the processes responsible for the spin relaxation in these lanthanide single-ion magnets.

[1] D.N. Woodruff, R.E.P. Winpenny, R.A. Layfield, Chem. Rev. 113 (2013) 5110. [2] 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. [3] J.D. Rinehart, J.R. Long, Chem. Sci. 2 (2011) 2078. [4] J.J. Baldoví, S. Cardona-Serra, J.M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, A. Palií, Inorg. Chem. 51 (2012) 12565.