Investigation of Thermal and Light-induced Spin State Transitions in Mn^{3+} and Fe^{3+} Complexes by Continuous Wave EPR

Hill, S., (NHMFL & FSU, Physics), Kühne, I.A. (University College Dublin, Ireland); van Tol, J., Ozarowski, A., Krzystek, J. (NHMFL); Morgan, G.G. (University College Dublin)

Introduction

The overall goal is to study the magnetic and electronic properties of transition metal-organic compounds which can be thermally and/or optically switched between different spin states. The compounds contain either Mn^{3+} which can be thermally switched between the S = 1 and S = 2 states, or Fe^{3+} which can be both thermally and optically switched. To date there are no reported EPR studies on following the S = 1 to S = 2 transition in Mn^{3+} and none on following the Light Induced Excited Spin State Trapping (LIESST) technique in Fe^{3+}. The aim for the Mn^{3+} studies was to establish the sign and magnitude of the zero field splitting and to determine if the transition could be followed by EPR. The aim for the Fe^{3+} was to determine if EPR was a viable technique to follow LIESST.

Experimental

High- field EPR spectra were collected on samples of three Mn^{3+} and one Fe^{3+} compounds using the 12.5 T and 15/17 T SC magnets in the EMR facility associated with the heterodyne and homodyne spectrometers, respectively. Spectra for the Fe^{3+} sample were also collected at 10 K while irradiating it with a white light source.

Results and Discussion

The main outcome of the experiments conducted during the reporting period is the observation that the magnitude and sign of the zero field splitting of the Mn^{3+} complexes changes during the transition. This was studied in depth on compound **1** which shows a sharp thermal transition from an S = 2 state at RT to a mixed S = 1/S = 2 state below 50 K, **Fig.1** (left). Thermal switching is accompanied by opening of a wide (20 K) hysteresis window and pulsed magnetic field switching between the two phases was also investigated at the NHMFL in LANL in parallel experiments. Fitting the data for the Mn^{3+} complex over multiple frequencies enabled extraction of D values of around -1.5 cm^{-1} for the S = 2 state and around +20 cm^{-1} for the S = 1 state. A second important outcome was demonstrating that LIESST could be achieved at 10 K and followed by EPR using a range of microwave frequencies and variable field in the Fe^{3+} sample.

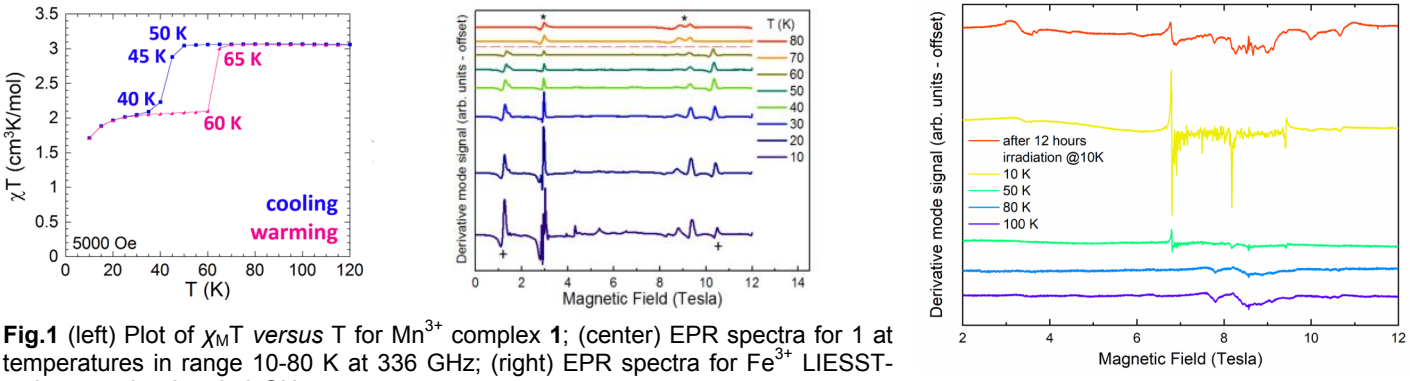

Fig.1 (left) Plot of $\chi_M T$ *versus* T for Mn^{3+} complex **1**; (center) EPR spectra for 1 at temperatures in range 10-80 K at 336 GHz; (right) EPR spectra for Fe^{3+} LIESST-active complex **2** at 240 GHz.

Conclusions

The observation of a change in the sign of D which accompanies the spin state change in one of the Mn^{3+} compounds is significant and further examples should be studied to establish the prevalence of this change and to enable complete magneto-structural analysis. Following the LIESST effect in the Fe^{3+} sample also requires further experiments using a range of wavelengths in the visible region.

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