High Field EPR Study of Novel 3*d*-4*f* Heterobimetallics

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Introduction

Synthesis of new 3*d*-4*f* heterobimetallics is of increasing scientific interest due to their potential applications in technology. Specifically, these novel materials find importance in the realization of some of the strongest known magnets [1,2] which owe their magnetic behavior mostly to the component lanthanide's unpaired 4*f* electrons and thus vary across the periodic table [3]. Incorporation of 3*d* transition metals in lanthanide compounds promotes interesting additional properties such as electronic conduction and thermochromism [4]. We have synthesized a new 3*d*−4*f* heterobimetallic family of compounds containing rare earth and transition metals, of the general formula, $X_2Cu(TeO_3)_2(SO_4)_2$ (X = Eu, Gd, Sm, Tb, Tm, Yb, Dy, Y), using hydrothermal synthesis and initiated high-field EPR to study their structure and magnetic properties [5].

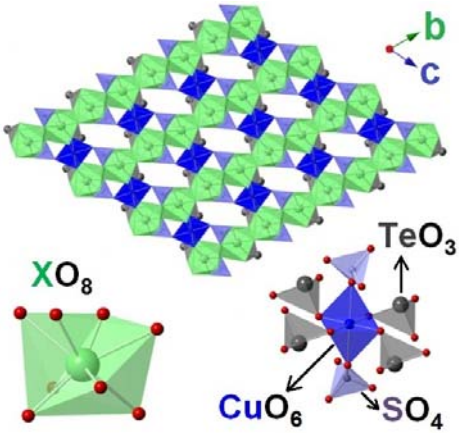

Figure 1 Crystal structure of $X_2Cu(TeO_3)_2(SO_4)_2$ (see text).

Experimental

Q band (34 GHz) powder EPR spectra were measured using a Bruker Elexsys 500 spectrometer available at FSU Chemistry Department. Variable temperature HFEPR powder spectra at 240 GHz were measured using a heterodyne spectrometer employing a 12.5 T superconducting magnet at NHMFL.

Results and Discussion

X-ray diffraction studies revealed that the crystal structures are isotypic forming a three-dimensional framework (Fig. 1). Powder EPR measurement on the Eu-analog at Q band (34 GHz) showed a spectrum characteristic of Cu^{2+} (S = 1/2) in an axially symmetric local environment (Fig. 2 – Inset), whereas at high frequency (240 GHz), the spectrum split into three separate peaks indicating rhombic local symmetry around the Cu^{2+} center. Comparison of spectra in Fig. 2 clearly depicts the significant improvement in spectral resolution at high fields. Thus HFEPR is an invaluable tool essential for studying these novel materials. Similar systematic data have been obtained on several related compounds; detailed analysis is in progress.

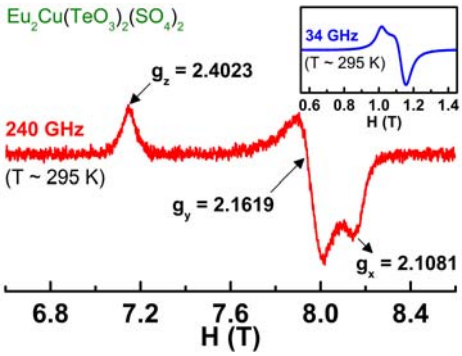

Figure 2 High-Frequency (240 GHz) powder EPR spectrum of $Eu_2Cu(TeO_3)_2(SO_4)_2$ at 295 K. (Inset: 34 GHz spectrum at 295 K).

Conclusions

HFEPR studies of a new family of 3*d*-4*f* heterobimetallic complexes shows the unique power of this technique for probing the electronic structure of this unique class of lanthanide and actinide based materials.

Acknowledgements

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References

[1] Zhao, B., *et al*., J. Am. Chem. Soc., **126**, 3012-3013 (2004)
[2] Volkringer, C., *et al*., J. Am. Chem. Soc., **134**, 1275-1283 (2012)
[3] Habib, F.; *et al.*, Chem. Soc. Rev., **42**, 3278-3288 (2013)
[4] Morita, Y., *et al*., Nature Mater., **7**, 48-51 (2008)
[5] Lin, J., *et al*., in preparation, (2014)