Electron Paramagnetic Resonance Characterization of a Polyoxopalladates Compound $[MnO_8Pd^{II}_{12}As_8]^{n-}$

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Introduction

Polyoxometalates (POMs) comprise a large class of nanosized, polynuclear metal-oxo anions that exhibit a wide compositional and structural diversity as well as a broad range of physical and chemical properties making them attractive for applications in different areas such as catalysis, medicine, magnetism, bio- and nanotechnology [1]. A total of 16 discrete polyoxopalladates(II) $[MnO_8Pd^{II}_{12}As_8]^{n-}$ (**MnPdAs**), with a metal ion Mn encapsulated in a cuboid shaped $\{Pd_{12}O_8As_8\}$ cage, have been synthesized. We report the High Frequency Electron Paramagnetic Resonance (HF-EPR) characterization of this compound.

Experimental

The samples were prepared by the Kortz group at Jacobs University, Germany. High field EPR measurements at 406.4 GHz were done on the home-built homodyne instrument at the National High Field Magnetic Laboratory, Tallahassee, FL.

Results and Discussion

Figure 1 shows typical HF-EPR spectra of **MnPdAs** taken at the very high frequency of 406.4 GHz and at various temperatures ranging from 290 K down to 4.5 K. The main feature of these spectra at temperatures higher than 50 K is the sextet of peaks centered at a *g*-value close to 2.00, with an equal spacing of about 85 G between the individual lines. This is a confirmatory evidence that the ground state of the metal ion has its orbital angular momentum *L* quenched and its nuclear spin (*I*) is 5/2, identifying the metal ion as Mn^{2+} (as expected). Whereas the sharp features arise from the $m_S = -1/2$ to $m_S = +1/2$ transition of the Mn^{2+} $S = 5/2$ state, the broader features are due to the other 4 allowed transitions in this sextet.

Due to the lattice disorder especially at low temperatures, a distribution of zero-field splitting values can be expected. The origin of the line broadening was attributed to the so-called "*D*-strain" phenomenon, which leads to a line broadening for a $m_S \rightarrow m_S + 1$ transition proportional to $(2\, m_S + 1)\Delta D$, where ΔD is the width of the distribution of the zero field splitting parameter *D*. Computer simulations using this model proved quite satisfactory, as can be noted from **Figure 2**.

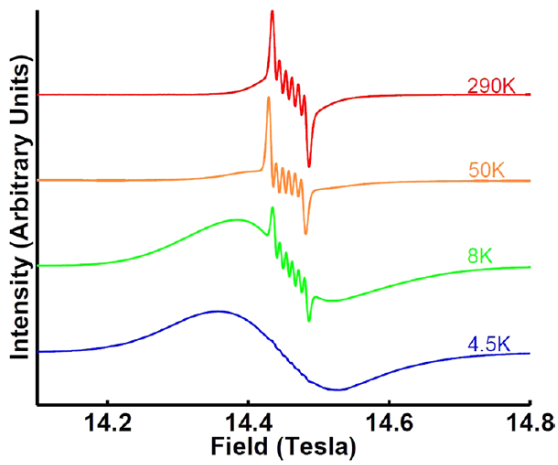

Figure 1. EPR spectra at various temperatures.

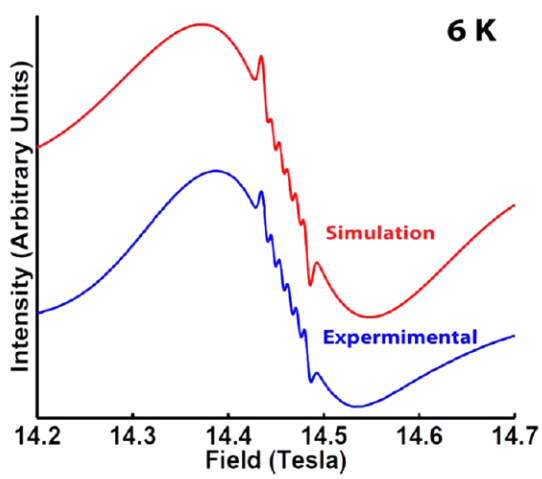

Figure 2. EPR spectra at 6 K and its simulation.

Conclusions

HF-EPR has confirmed the $S = 5/2$ ground state of **MnPdAs**. The lattice distortion has been detected and theoretically simulated. The work has been published in Inorg. Chem. in 2012 [3].

Acknowledgements

All EPR measurements were made at NHMFL, supported by NSF Cooperative Agreement No. DMR-0654118, by the State of Florida, and the DOE.

References

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