HFEPR of Magnetic Materials with Unusual Optical Properties: $YIn_{1-x}Mn_xO_3$

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Introduction

A new class of magnetic materials has recently been prepared by Subramanian and co-workers [1, 2]. These materials are based on $YInO_3$, in which the diamagnetic In(III) ions are replaced by paramagnetic ($3d^4$, $S = 2$) Mn(III), in trigonal bipyramidal (tbp) geometry, to give [$YIn_{1-x}Mn_xO_3$], where $0 \leq x \leq 1$. These doped systems exhibit an intense blue color over the range of $0 < x \leq \sim 0.2$ (see **Figure 1**), and are being developed for use as blue pigments that are more robust and environmentally "friendly" than those in current commercial use.

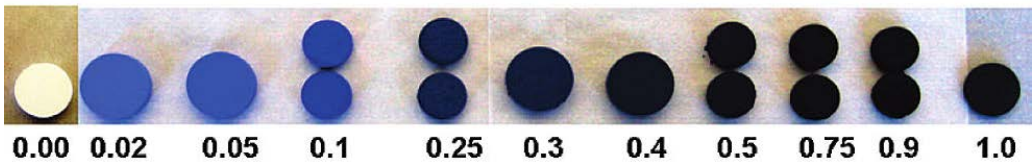

Figure 1. Powders of $YIn_{1-x}Mn_xO_3$, as a function of x. Pure $YInO_3$ is white as expected; low doping gives an intense blue color.

Experimental

The Millimeter and Submillimeter Wave Facility and the 25-T resistive "Keck" magnet at NHMFL were used to measure HFEPR spectra of powdered $YIn_{1-x}Mn_xO_3$, with x = 0.05, 0.1, 0.2, and 0.5. As previously seen, higher doping levels dilution led to excessive line broadening due to interionic magnetic interactions, while very low levels unnecessarily reduced S/N.

Results and Discussion

We followed the project initiated and reported in 2011 by performing HFEPR experiments on samples differing by the Mn(III) concentration x. All samples showed strong and well-defined EPR responses in the 80 – 700 GHz frequency range, and in a wide temperature range from liquid helium to room temperature. **Figure 2** shows the field/frequency dependence of HFEPR resonances (recorded at 4 – 10 K) for $YIn_{0.95}Mn_{0.05}O_3$ together with a computer fit of the pattern. This process gave the $S = 2$ spin Hamiltonian parameters for the Mn(III) site in these materials, which are practically independent of either x (here, 0.05) or temperature: $D = +2.965(3)$ cm^{-1}, $|E| = 0.006(1)$ cm^{-1}, $g_\perp = 1.987(2)$, $g_{||} = 2.008(5)$.

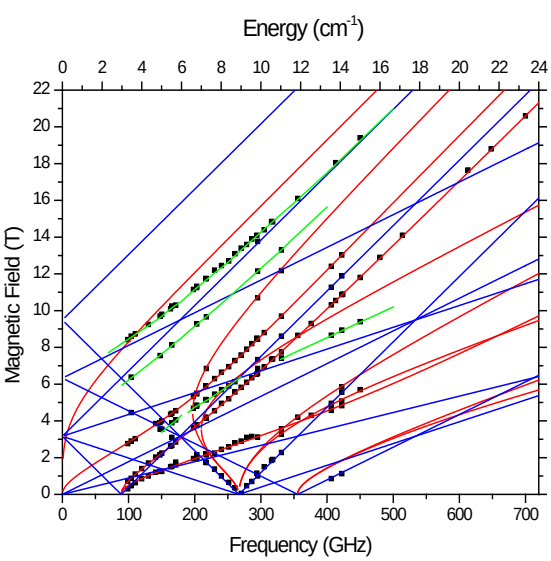

Figure 2. Field/frequency map of resonances in $YIn_{0.95}Mn_{0.05}O_3$ recorded at 4.2 – 10 K. The squares are experimental turning points while the lines were drawn using best-fitted spin Hamiltonian parameters as in the text. Red lines: perpendicular; blue lines: parallel; green lines: off-axis turning points.

Conclusions

The $YIn_{1-x}Mn_xO_3$ materials have shown great potential for HFEPR investigations. Future work will involve relating these magnetic parameters derived from HFEPR to their optical properties, and to analogous properties of other Mn(III) systems, which rarely exhibit tbp geometry.

Acknowledgements

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References

[1] Smith, A.E., *et al.*, J. Am. Chem. Soc., **131**, 17084–17086 (2009).

[2] Mizoguchi, H., *et al.*, Inorg. Chem., **50**, 10–12 (2011).