HFEPR of Magnetic Materials with Unusual Optical Properties: $YIn_{1-x}Fe_xO_3$

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Introduction

A new class of magnetic materials has recently been prepared by Subramanian and co-workers [1]. These materials are based on $YInO_3$, in which the In^{3+} ions are replaced by M^{3+} to give $[YIn_{1-x}M_xO_3]$, where $0 \le x \le 1$, and $M^{3+} = Mn^{3+}$ ($3d^4$, $S = 2$) [2], Fe^{3+} ($3d^5$, $S = 5/2$) [3]. $YInO_3$ is white, as expected for a closed shell system (Y^{3+}, $[Kr]4d^0$; In^{3+}, $[Kr]4d^{10}$, both $S = 0$). The doped systems exhibit intense colors: blue for Mn and yellow to orange to red to red-brown for Fe, as a function of x. These materials already have applications as pigments and as IR-reflective screens. Their structure is shown in **Figure 1**. The relation between their optical and magnetic properties is thus of great interest.

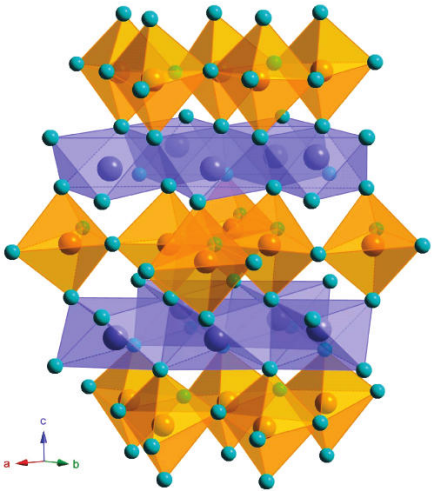

Figure 1. Structure of $YIn_{1-x}Fe_xO_3$ (Y, blue; In and Fe, orange; O, turquoise spheres).

Experimental

The EMR Facility and its 15/17-T superconducting magnet was used to record HFEPR spectra of powdered $YIn_{1-x}Fe_xO_3$, with $x = 0.1 – 0.5$.

Results and Discussion

We have often had difficulty in observing satisfying HFEPR spectra from complexes of Fe^{3+} (and of Fe^{2+}), but not so here. High-quality spectra, in terms of S/N and linewidth, were recorded for the whole range of Fe concentrations, and in a wide temperature range from liquid helium to room temperature. Higher dilution reduced the S/N and lower dilution led to excessive line broadening due to spin-spin magnetic interactions. **Figure 2** shows an HFEPR spectrum of Fe^{3+} at 203.2 GHz and 10 K. The frequency dependence of HFEPR resonances has been mapped (not shown) and computer fitting of this pattern allowed determination of the $S = 5/2$ spin Hamiltonian parameters for the Fe^{3+} sites. For example, the sample with $x = 0.1$ yields: $D = –1.095(2)$ cm^{-1}, $E = 0.003(4)$ cm^{-1}, $g_\perp = 2.007(1)$, $g_\parallel = 2.004(3)$. The current study complements the relatively few ferric systems investigated by HFEPR, and is the first of the trigonal bipyramidal geometry.

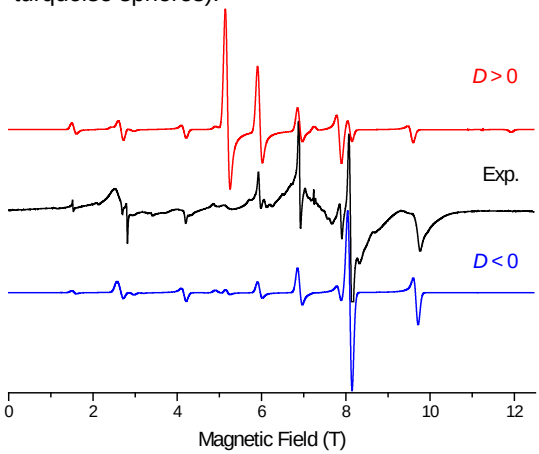

Figure 2. HFEPR spectrum of $YIn_{0.9}Fe_{0.1}O_3$ recorded at 203.2 GHz and 10 K (black trace) together with powder pattern simulations using spin Hamiltonian parameters as in text. Red trace: positive D; blue trace: negative D.

Conclusions

The $[YIn_{1-x}Fe_xO_3]$ pigments have shown great promise for HFEPR investigations. Future work will involve the relation of the parameters derived from HFEPR with the optical properties of these materials and with other Fe^{3+} systems.

Acknowledgements

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References

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[2] Mizoguchi, H., *et al.*, Inorg. Chem., **50**, 10-12 (2011).
[3] Jiang, P., *et al.*, Inorg. Chem., **50**, 5858-5860 (2011).