High-Frequency and -Field EPR Study of the Magnetochemical Standard $HgCo(NCS)_4$

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Introduction

Calibration of magnetochemical hardware is traditionally based upon the mercury(II)-tetrakis(iso-thiocyanato)cobaltate, $HgCo(NCS)_4$. Several basic papers have been devoted to this problem including the most recent publication that utilized the powder susceptibility data, along with the single-crystal data taken by a SQUID magnetometer, in order to retrieve the set of magnetic parameters, such as the axial zero-field splitting parameter *D*, the magnetogyric factor g_{iso}, (g_z and g_x for a single crystal) and eventually the molecular-field correction *zj* [1]. We feel there is a need of updating these data using HFEPR which is much more accurate than bulk magnetometric techniques in determining the magnetic parameters.

Experimental

The $HgCo(NCS)_4$ sample was purchased from Alfa Aesar, ground and pressed into an *n*-eicosane pellet. The temperature was 10 K, and frequency varied from 100 to 420 GHz using the VDI source of the homodyne spectrometer associated with the 15/17 T SC magnet at the EMR Facility.

Results and Discussion

$HgCo(NCS)_4$ produced HFEPR spectra distinctly characteristic for high-spin (S = 3/2) cobalt(II) (Fig. 1). Although particular resonances were broad, they could be successfully simulated with a conventional spin Hamiltonian using the following parameters: S = 3/2, D = +5.50(5) cm^{-1}, E = 0.0(1) cm^{-1}, $g_{\perp}$ = 2.15(5), $g_{||}$ = 2.20(5). The zero-field splitting (zfs) tensor is thus axial within the error determined by the line width, and *D* is positive.

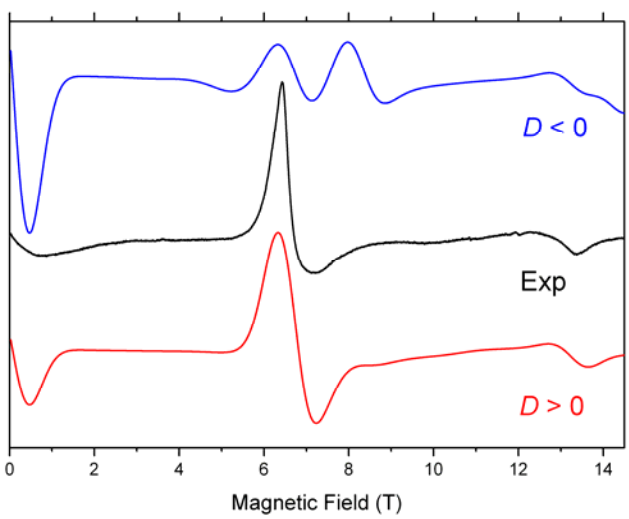

Figure 1. HFEPR spectrum of a $HgCo(NCS)_4$ pellet recorded at 328.8 GHz and 10 K (black trace) along with simulations using spin Hamiltonian parameters as in text. Blue trace: negative *D*; red trace: positive *D*. The latter reproduces much better the experiment.

Conclusions

The new HFEPR data largely confirm the previous results obtained by non-resonant methods. The zfs parameters are typical for high-spin Co^{II} in a tetrahedral coordination. The large line width makes it difficult to improve on those results. The origin of the line width may lie in the small size of the thiocyanate ligands as small ligands typically have many degrees of freedom, which leads to a structural disorder at low temperatures. An alternative explanation is also based on the small size of the ligands as they do not provide good magnetic isolation of the particular Co^{II} centers, which may result in extensive spin-spin interactions.

Acknowledgements

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References

[1] Nelson, D; ter Haar, L.W., Inorg. Chem., **32**, 182-188 (1992).