HIGH-FIELD, HIGH-FREQUENCY EPR STUDY ON IRON(II) HEXAFLUOROSILICATE HEXAHYDRATE, FeSiF₆·6H₂O

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Introduction

Iron(II) is ubiquitous in nature, in a wide range of coordination environments. The high-spin state of the Fe²⁺ ion (3d⁶, S = 2) is difficult to investigate by EPR owing to the very large zero-field splitting. Consequently, successful EPR of Fe(II) has been very rarely reported¹⁻⁴. The title compound was investigated by far-infrared magnetic resonance in the past⁴, but no g values or fourth-rank zero-field splitting (ZFS) parameters were determined.

Experimental

100 mg pellets of the freshly prepared title compound were investigated using the transmission homodyne spectrometers of the EMR facility (with a 17-Tesla superconducting magnet) and the Mm- and Sub-Mm Wave Facility (with a 25-Tesla resistive magnet), at temperatures 4.2-30 K.

Results and Discussion

The following parameters of the spin Hamiltonian

\[ H = \mu_B B g \cdot S + D (S_x^2 - \frac{1}{3} S(S+1)) + E (S_y^2 - S_z^2) + B_{4i}^0 O_{4i}^0 + B_{4i}^2 O_{4i}^2 + B_{4i}^4 O_{4i}^4 \] ¹

were found by fitting the frequency-magnetic field dependencies shown in Fig. 1: \( g_x = 2.083(7) \), \( g_y = 2.131(8) \), \( g_z = 2.000(2) \), \( D = +11.97(1) \) cm⁻¹, \( E = +0.653(4) \) cm⁻¹, \( B_{4i}^0 = 0.0016(1) \) cm⁻¹. Parameters \( B_{4i}^2 \) and \( B_{4i}^4 \) were found to be equal to zero within the error limit.

Conclusions

Spin Hamiltonian parameters for an iron(II) compound were successfully measured. One of the fourth-rank ZFS parameters, \( B_{4i}^0 \) was found to be not equal to zero. The zero-field transition energies reported in [4] can be better reproduced with our parameters than in the original paper⁴. Interpretation of the spin Hamiltonian parameters is in progress.

Acknowledgements

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References