Single-Crystal High-Pressure, High-Frequency EPR of Cobalt(II) Dimers

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Introduction

Exchange-coupled cobalt(II) dimers containing ions in a distorted octahedral environment are extremely difficult to model due to first-order spin-orbit coupling. An unusual switch in the sign of the exchange interaction has been observed between $[Co_2(OH_2)((CH_3)_3COO)_4((CH_3)_3COOH)_4]$ (**1**) and $[Co_2(OH_2)((CH_3)_3COO)_4((CH_3)_3COOH)_2(py)_2]$ (**2**), where the only difference is the substitution of two terminal pivalic acid ligands for pyridine. A semi-empirical model for the system has been formed using data obtained from Inelastic Neutron Scattering (INS), powder high-frequency high-field electron paramagnetic resonance (HFEPR), magnetization and *ab initio* studies, but the root of the phenomenon has yet to be fully determined [1]. A useful experiment would be to compare the effects of chemical changes versus geometric changes, since going from **1** to **2** changes both simultaneously. Pressure can be used to induce a change in geometry without altering chemistry.

Experimental

High-pressure EPR measurements were carried out on an oriented crystal at 0 kbar and 9.2 kbar using diamond anvil cells with gaskets made of zylon fibers. Flourinert was used as the pressure transmitting medium and a ruby luminescence method was applied to calibrate the pressure in-situ. The sample size (350 x 200 x 100 μm^3) was constrained by the diamond culet size, which was 1 mm in this case. The frequency range of 50-300 GHz was covered at temperatures from 2 to 20 K.

Results and Discussion

The HFEPR of oriented compound **2** at 0 kbar and 9.2 kbar shows a small shift in the position of the multiple resonance peaks. Since Co(II) ions have large spin orbit coupling, the small shifts in the exchange coupling can lead to large changes in the anisotropies of the ions. Hence further studies on increasing the pressure will give more insight into the anisotropically coupled Co(II) dimers.

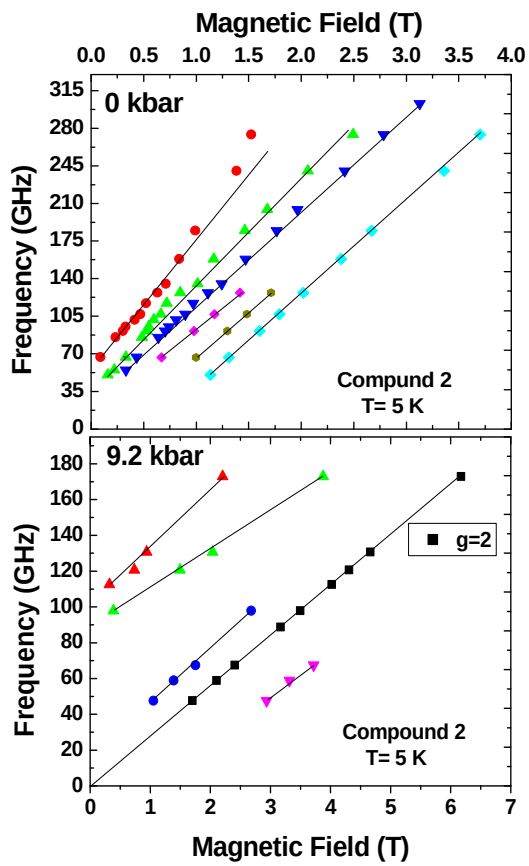

Figure 1. Frequency vs magnetic field plot of the EPR resonances in(2) at 0 kbar (top) and 9.2 kbar(bottom). The g = 2 peak corresponds to the impurity signal from diamond. Solid lines are guide to the eye.

Conclusions

Preliminary measurements at two different pressures appear to show significant differences in the electronic structure. Further measurements and data analysis are currently planned.

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References

[1] Boeer, A.B., *et al.*, Angew. Chem. Int. Ed., **50**, 4007-4011 (2011).