UNPRECEDENTED MAGNETIC ORDERING AND "METAMAGNETISM" OF AN *S* = 2 FERROUS DIMER: SUB-THZ SPECTROSCOPY OF $[dmpipzH_2][Fe_2Cl_4(H_2O)_6]Cl_2$

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Introduction

$[dmpipzH_2][Fe_2Cl_4(H_2O)_6]Cl_2$ **(1)** consists [1] of a 3-dimensional array of 1,4-dimethyl-piperazinium dications, ($dmpipzH_2^{2+}$), *neutral* ferrous dimers composed of mer-$Fe(H_2O)_3Cl_3$ chromophores and two ionic chlorides. From 80 to 5 K, μ gradually decreases from the spin only value of Fe^{2+} (4.9μ_β/Fe) to 3μ_β/Fe, behavior typical of weak intra-dimer exchange, $J(dimer)/k_B \sim -0.5\ K$. Below ~5 K, μ decreases rapidly to ~ 0.6μ_β at 1.4 K, *coincident* with the onset of magnetic hyperfine splitting ($H_{internal}$ = 14 T) of its zero field Mössbauer spectrum. Long range magnetic order is further confirmed by AC susceptibility and heat capacity data that indicate that **(1)** has an uncanted ground state (χ"=0), $T_N \sim 4.3$ K. This behavior is unprecedented for ferrous dimers and is the result of hydrogen bonded super-exchange interactions and the small value of J(dimer). More definitive evidence for the antiferromagnetic nature of the 3D magnetic ground state comes from the observation of a "metamagnetic" phase transition at ~1.5 T in the (DC) field dependence of M(DC), M(AC) and heat capacity to 9 T.

Experimental

In order to further investigate the magnetic properties of **(1)** we took advantage of the mm and sub-mm spectroscopy facility at the NHMFL in conjunction with the resistive Keck magnet.

Results and Discussion

We observed an unusual, sharp, non-resonant decrease in the sub-THz wave radiation absorption occurring at 1.85 K upon sweeping the field up at 1.45 T (Fig. 1). The magnetic field value of the transition point is independent of frequency in the 150 – 700 GHz range and exhibits a hysteresis-type behavior depending on the direction of the field sweep. We attribute this phenomenon to the metamagnetic transition observable by other techniques at the same field value, and tentatively explain it as caused by the different propagation properties (such as different ε) of the sub-THz waves in the antiferromagnetic phase (below the metamagnetic transition) compared to the field-induced paramagnetic phase above the transition field. ESR (resonant) transitions were also observed in the same frequency range, and over a 4 – 25 T field range (not shown). These, however, can be tentatively attributed to a high-spin ferric (Fe^{3+}) impurity, and not the bulk properties of the crystal.

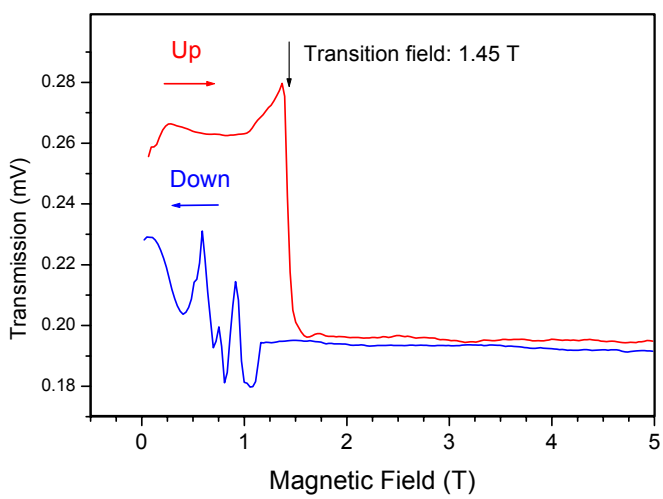

Figure 1. Sub-THZ wave transmission through a powdered sample of **(1)** at 1.85 K and 225 GHz as a function of magnetic field.

References

[1] S. I. Troyanov, *et al.,* Z. Anorg. Allg. Chem. **625**, 806 (1999).