MAGNETIC FIELD DEPENDENCE OF ELECTRONIC EXCITATIONS IN PARAMAGNETIC ANALOGS OF THE NENB HALDANE COMPOUND

V.C. Long, J.R. Montague, A.C. Kozen (Colby College, Physics); X. Wei (NHMFL, Visible Optics); B.R. Landry, M.M. Turnbull (Clark University, Chemistry); C.P. Landee (Clark University, Physics); R.D. Willett (Washington State University, Chemistry)

Introduction

NENB, $Ni(en)_2NO_2BF_4$, is isostructural to the prototypical Haldane compound NENP, $Ni(en)_2NO_2ClO_4$ (en = $C_2H_8N_2$). Both have spin chains of S=1Ni^{2+} ions and a Haldane energy gap of ~1 meV. Earlier work on NENB [1] showed remarkable intensity changes of the electronic excitations above the critical field, $H_C \approx 10$ T. In particular, a Ni^{2+} *d-d* spin-forbidden transition is gradually suppressed by applied H and a Ni^{2+}-to-NO_2^- charge transfer transition is enhanced by H, for $H > H_C$. Compounds with isolated Ni^{2+} ion complexes, having similar electronic coordination but lacking the spin chains, can be considered paramagnetic analogs to the Haldane materials. Two such compounds are NEN3P, $Ni(en)_3(ClO_4)_2\,H_2O$, and NTNB, $Ni(tn)_2NO_2BF_4$ (tn = $C_3H_{10}N_2$). We have measured the field dependence of the electronic excitations in NEN3P and NTNB to compare the effect of the paramagnetic ground state on the absorption intensity modifications in applied field.

Experimental

We measured the optical transmittance of single crystals at 1 T steps up to 30 T in the bore of a DC electromagnet with the sample at T = 4.2 K. To highlight small changes in absorption intensities, we converted each transmittance spectrum to absorbance (A) and calculated the absorbance difference, A(H) - A(H = 0 T).

Results and Discussion

Figures 1 and 2 show the absorbance difference spectra for NEN3P and NTNB respectively. The insets show that intensity modifications in the spin forbidden band at ~12,800 cm^{-1} commence immediately above H = 0 T, in contrast to the Haldane compounds in which changes occur only above the critical field.

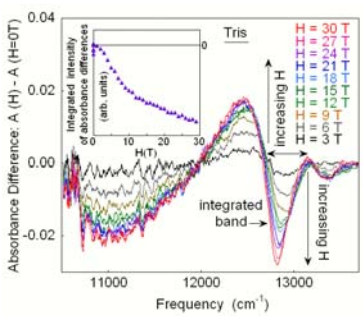

Figure 1. Near infrared absorbance difference spectra of $Ni(en)_3(ClO_4)_2$ H_2O at varying magnetic fields. The inset shows the integrated intensity (area) versus field of the band indicated by a double arrow.

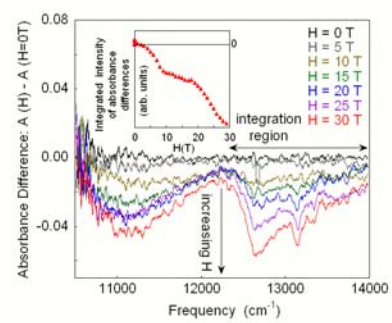

Figure 2. Near infrared absorbance difference spectra of $Ni(tn)_2NO_2BF_4$ at varying magnetic fields. The inset shows the integrated intensity (area) versus field of the band indicated by a double arrow.

Conclusions

Field dependence of the near infrared electronic absorptions appears to be a common property of Ni^{2+} ion compounds with octahedral N coordination, but the details of the intensity modifications depend on the magnetic ground state of the material.

Acknowledgements

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References

[1] Long, V.C., *et al*., Journal of Magnetism and Magnetic Materials, **272-276**, 968-969 (2004).

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