Magnetic Field-Induced Energy Shifts in Electronic Bands of Ni(II) Coordination Compounds

V.C. Long, Y.-H. Chou, I.A. Cross, A.C. Kozen, J.R. Montague (Colby College); S.A. McGill (NHMFL); K.R. Pearson (Fashion Institute of Technology); B.R. Landry, M.M. Turnbull, C.P. Landee (Clark University); R.D. Willett (Washington State University)

Introduction

The electronic excitations of Ni^{2+} in certain Haldane spin chains are sensitive to magnetic field *H*, with different excitations showing characteristic enhancement or suppression of the band intensities.[1] For comparison, we have studied the *H* sensitivity of electronic transitions in some Ni^{2+} coordination compounds: Ni(trimethylenediamine)$_2$(NO$_2$)$_2$, Ni(ethylenediamine)$_3$(ClO$_4$)$_2$ H$_2$O, and Ni(triethanol amine)$_4$(NO$_2$)$_2$. The three latter compounds can be taken loosely as paramagnetic analogs of the aforementioned Haldane compounds, Ni(ethylenediamine)$_2$NO$_2$ClO$_4$ (NENP) and Ni(ethylenediamine)$_2$NO$_2$BF$_4$ (NENB), since all have related electronic structures due to similar coordination of the Ni^{2+} ion.

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 4.2 K. Each transmittance spectrum was converted to absorbance (A) and the absorbance difference, AD = A(H) - A(H = 0 T) was calculated to highlight small field-dependent changes. See Ref. [1] for experimental details.

Results and Discussion

Figure 1 shows the derivative shaped AD spectra of the paramagnetic analog compounds, indicating that electronic band energies are shifting with applied *H*. For the sharply-defined *H*-sensitive features, such as the vibrational fine structure on the spin-allowed *d-d* band of Ni(trimethylenediamine)$_2$(NO$_2$)$_2$ (left) and the spin forbidden *d-d* band of Ni(ethylenediamine)$_3$(ClO$_4$)$_2$ H$_2$O (center), the energy shift can be quantified from the single beam absorbance (see insets).The substantial width and overlap of the *H*-sensitive band in Ni(triethanol amine)$_4$(NO$_2$)$_2$ precludes such a determination.

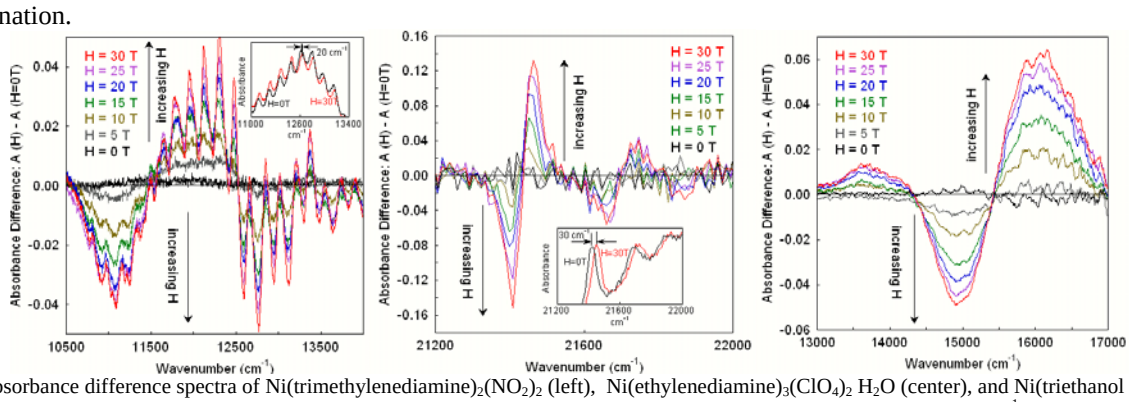

Fig. 1. Absorbance difference spectra of Ni(trimethylenediamine)$_2$(NO$_2$)$_2$ (left), Ni(ethylenediamine)$_3$(ClO$_4$)$_2$ H$_2$O (center), and Ni(triethanol amine)$_4$(NO$_2$)$_2$ (right) at the indicated fields. The insets (left and center) show the single beam absorbance at H = 0T and 30T and the 20-30 cm^{-1} blue shift between them.

Conclusions

Whereas the *H* sensitivity of electronic bands in the Haldane compounds consists solely of intensity changes, [1] the three paramagnetic analog compounds exhibit a response to applied *H* that slightly shifts the *d-d* bands to higher energy.

Acknowledgements

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References

[1] Long, V.C. *et al*., Physical Review B **76**, 024439 (2007).