Magnetometry Study of the *S* = 1 Chain $Ni(NCS)_2(Thiourea)_2$ with Bridging Thiourea

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Introduction

$NiCl_2(tu)_4$ [tu = thiourea = $CS(NH_2)_2$] has tetragonal symmetry and contains molecules with close Cl⋯Cl contacts along the crystallographically unique *c*-axis.[1] Quasi-1D Ni-Cl⋯Cl-Ni chains mediate a weak AFM exchange of 2.2 K but with a large *D*-value of ~9 K. Bose-Einstein condensation (BEC) of magnons has been reported to exist between critical fields of 2.2 and 11 T.[2] By means of chemical design, the halide can be replaced by thiocyanate (NCS^-) however, the thiourea ligands form bridges between Ni(II) sites leading to bi-bridged Ni-S_2-Ni chains as shown in Fig. 1.[3] The unique crystal structure and close Ni⋯Ni distances should lead to strong intrachain magnetic correlations. Weak interchain interactions are potentially mediated by (NC)-S⋯H-N hydrogen bonds. We measured the magnetization of $Ni(NCS)_2(tu)_2$ as a function of temperature and briefly report those findings here.

Experimental

Magnetometry measurements were conducted at the Pulsed-Field Facility of the NHMFL-Los Alamos using a Quantum Design Physical Property Measurement System equipped with a 15 T superconducting magnet. A powder sample with a mass of 18.5 mg was mounted on a brass sample holder and inserted into the cryostat. Data were collected upon cooling in a 0.1 T dc field down to 2 K. Diamagnetic corrections to the data were made.

Results and Discussion

Plots of $\chi(T)$ and $\chi(T)T$ are shown in Fig. 2.[4] A peak is readily observed at 11 K in $\chi(T)$ and the derivative curve shows a very sharp peak at 10.5 K which we ascribe to long-range magnetic order. On the low temperature side of the peak, $\chi(T)$ decreases very rapidly and reaches a nearly constant value of ~0.6 emu/mol. The plot of $\chi(T)T$ (inset of Fig. 2) shows a smooth increase upon cooling due to ferromagnetic correlations, reaching a maximum near 12 K. Below 12 K, $\chi(T)T$ decreases abruptly due to a transition to long-range antiferromagnetic order. Because the title compound contains S = 1 Ni(II) in a near-octahedral coordination environment, zero-field splitting (D) is also expected. As such, the high magnetic ordering temperature could be induced not only by weak interchain couplings but also D and/or spin-exchange anisotropy.

Conclusions

$Ni(NCS)_2(tu)_2$ presents interesting *T*-dependence of the magnetization such that long-range magnetic order is clearly evident below 10.5 K. Additional features suggest the co-existence of *ferro*- and *antiferro*magnetic interactions that should be investigated in more detail. Work is continuing along these lines.

Acknowledgements

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References

[1] Lopez-Castro, A. and Truter, M. R., J. Chem. Soc., 1309 (1963).
[2] Zapf, V., *et al*., Phys. Rev. Lett., **96**, 077204 (2006).
[3] Nardelli, M., *et al*. Acta. Cryst. **20**, 349-353 (1966).
[4] Manson, J. L., *et al*. work in progress.

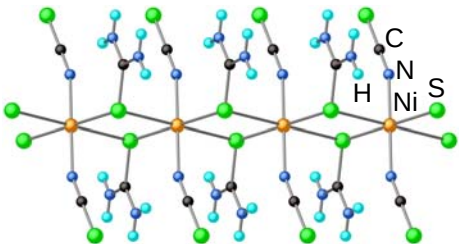

Fig.1. Crystal structure of polymeric $Ni(NCS)_2(tu)_2$.

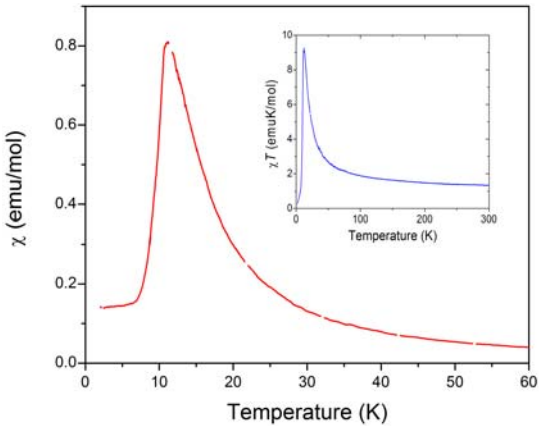

Fig.2. $\chi(T)$ and $\chi(T)T$ data for $Ni(NCS)_2(tu)_2$ obtained at 0.1 T.