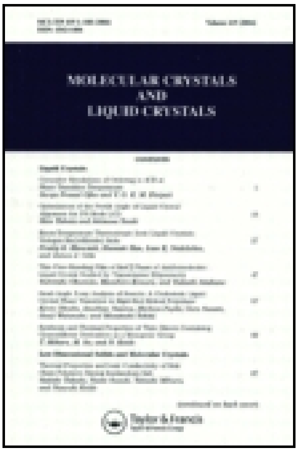

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Single Crystal Magnetic Measurements of the Molecular Magnet $NH_4Ni(mnt)_2.H_2O$

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SINGLE CRYSTAL MAGNETIC MEASUREMENTS OF THE MOLECULAR MAGNET $NH_4Ni(mnt)_2.H_2O$

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Abstract We report measurements of the magnetic properties of the molecular magnet $NH_4Ni(mnt)_2.H_2O$. The magnetic exchange in this salt is ferromagnetic below 100K, with a Weiss constant of 7 K. Long range magnetic ordering is observed below 5 K. Single crystals of this salt have been studied down to 2 K in a SQUID magnetometer. The salt is found to have hard and easy magnetisation directions. Magnetisation of 1800 emuG/mol at 2 kOe was measured at 2 K for magnetic fields applied perpendicular to the molecular stacking axis.

INTRODUCTION

There is interest in the electronic structure of molecular transfer salts formed with $M(mnt)_2$ complexes, where (mnt) is a maleonitrile dithiolate ligand and M is a square-planar coordinated transition metal. The structure of the nickel complex studied here is shown in figure 1. Complexes of the type $M'M(mnt)_2$, which have M' and $M(mnt)_2$ in a 1:1 stoichiometry and form segregated stacks of donor and acceptor, are usually found to be dimerised, insulating and antiferromagnetic . These include the Li^+, Na^+, K^+, Rb^+ and Cs^+ salts of the $Ni(mnt)_2$ anion[1,2]. The ammonium salt was investigated by Issett et al[3], and also by Underhill and Clemenson[4], and was found to show antiferromagnetic interactions. However studies of more recently produced samples of this material show ferromagnetic exchange at low temperatures [5].

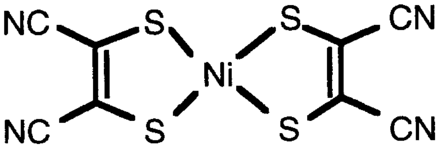

FIGURE 1 Molecular stucture of $Ni(mnt)_2^-$

The structure of this salt has been reported by Isett et al [4] and also by Hursthouse et al [1,6]. As with other members of the M'M(mnt)2 family of materials the Ni(mnt)2 complexes are arranged in one-dimensional stacks. One interesting feature of the room temperature structure is that the Ni(mnt)2 molecules in the stacks are equidistant. This is unusual as integral charge transfer salts usually show strong dimerisation.

PREPARATION AND CHARACTERISATION

The $NH_4Ni(mnt)_2H_20$ crystals investigated here were prepared by a modification of the method described by Issett et al [3]. Two platinum electrodes were placed in a solution of urea and $[NH_4]_2[Ni(mnt)_2]$ in deionised, degassed water under a nitrogen atmosphere and connected to a voltage source of 1.0 V. The crystals then grew over a period of eight days at the anode. Crystals grew as elongated platelets, and X-ray measurements on crystals selected from the batches used in this work indicate that the unit cell of the material prepared and investigated here is the same as that prepared previously [7].

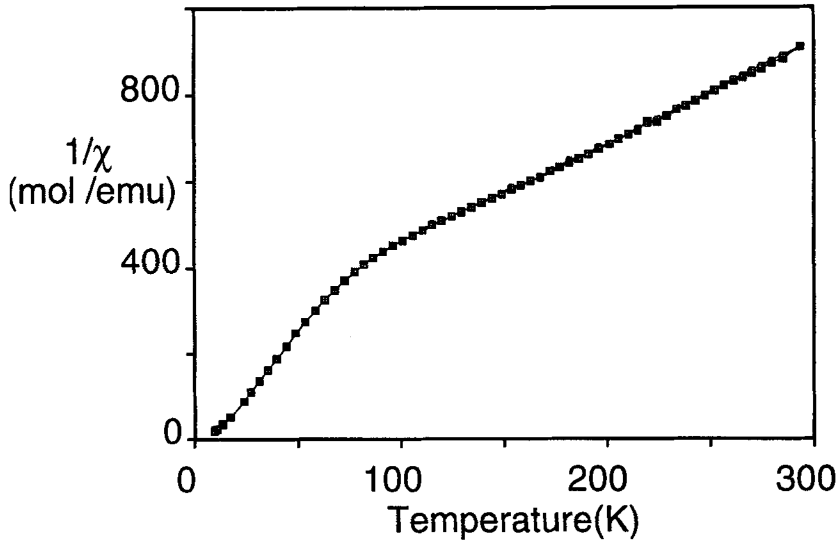

Figure 2 Susceptibilty of polycrystalline $NH_4Ni(mnt)_2.H_2O$

The susceptibility of polycrystalline samples was measured using the same Faraday balance as used in earlier studies [5]. We found similar magnetic behaviour, with a paramagnetic susceptibility above 120 K that is consistent with antiferromagnetic exchange, but with a cross-over below this temperature to ferromagnetic behaviour. Results as measured in the present work are shown in figure 2. Fitting a Curie-Weiss law $\chi = C/(T-\theta)$ to the susceptibility data above 100K gives a negative Weiss constant (θ) indicative of antiferromagnetic coupling and a Curie constant consistent with one g=2 spin $^1/_2$ electron per $Ni(mnt)_2$ formula unit. As the $1/\chi$ plot in Figure 1 shows there is, however, a change in the magnetic behaviour as the sample cools below 100K. A fit to the data below 100K gives a positive intercept with the temperature axis leading to a Weiss constant of 8K but a Curie constant consistent with 0.4-0.5 g=2 spin $^1/_2$ per molecular unit. At low temperatures the susceptiblity deviates from the simple Curie-Weiss law due to long range ferromagnetic ordering.

SQUID MEASUREMENTS

To investigate the properties of $NH_4Ni(mnt)_2.H_2O$ below the magnetic ordering temperature (5 K) single crystals were studied using a Quantum Design SQUID Magnetometer.

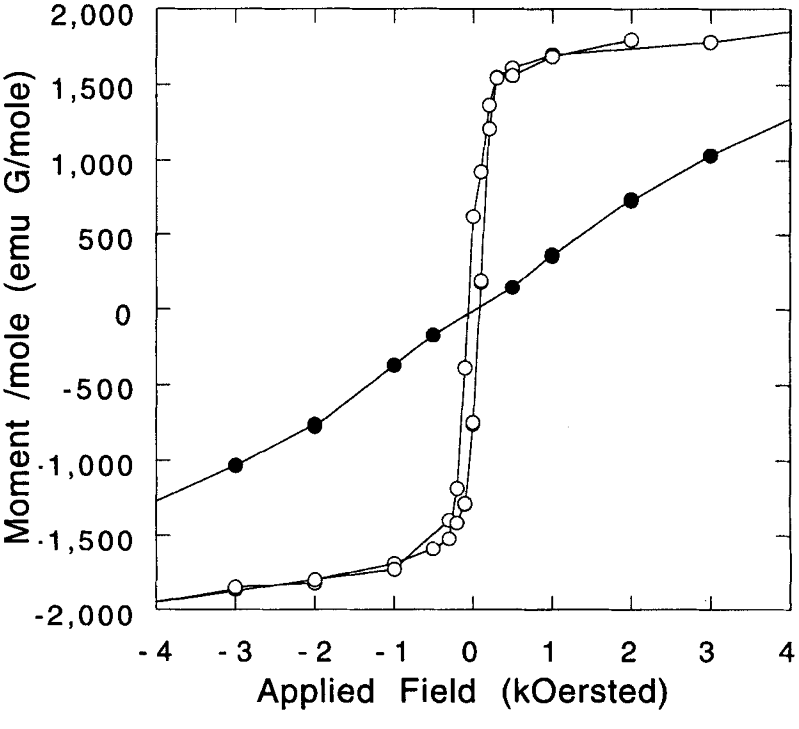

FIGURE 3 Magnetisation curves of a 11µg single crystal of $NH_4Ni(mnt)_2.H_2O$ taken at 2K. Solid data points are with the applied field parallel to the b-axis (stacking axis) and the open circles are for the applied field perpendicular.

Magnetisation versus H field plots measured at 2 K are shown in figure 3. The experiment was performed by securing the crystals to a quartz ESR tube with a light smearing of silicone grease. This provided a diagmagnetic background that was sufficiently small to see the signal from the small single crystals. Magnetisation curves were then taken with the long axis of the crystal parallel and perpendicular to the applied field. For crystals of $NH_4Ni(mnt)_2.H_2O$ the long crystal axis is the b axis along which the $Ni(mnt)_2$ complexes stack [7].

Measuring the moment parallel to the long axis produced a hard magnetisation curve with a monatomic increase of the magnetic moment with field. With the stacking axis of the crystal perpendicular to the field the magnetisation is very different. This magnetisation curve shows hysteresis with a coercive field of around 100 Oersted and magnetisation of 1800 emuG/mol at 2000 Oersted. If we assume that g=2 then this saturation magnetisation corresponds to around one third of a spin $^1/_2$ electron per $Ni(mnt)_2$ complex. Increasing the field further to 50 kOersted gives a measured magnetisation of 2200 emuG/mol.

DISCUSSION

The results presented above provide clear evidence of a long-range-ordered ferromagnetic state in $NH_4Ni(mnt)_2.H_2O$ below 5 K. Ferromagnetic ordering is very unusual for a charge transfer salt of this type. We would expect the intermolecular exchange within the stacks to be antiferromagnetic, as is found to be the case in similar salts[1,2].

The number of spins calculated from the Curie-Weiss fit to polycrystalline susceptibility measurement of $NH_4Ni(mnt)_2.H_2O$ below 100K is around 0.4 spins per molecular unit. This is smaller than expected and does not match the number of spins deduced from a Curie-Weiss fit above 100K when the exchange is antiferromagnetic. However we note that it does match the number of spins seen in the saturation magnetisation measured in the SQUID magnetometer on a single crystal at 2K.

The 2K magnetisation measurement also shows that crystals of $NH_4Ni(mnt)_2.H_2O$ have a hard and easy magnetisation direction due to spin orbit coupling. This preferred spin orientation is consistent with a material with molecular stacks which we would expect to be anisotropic.

The change in sign of the magnetic coupling between molecular units with temperature could be due to a structural transition at around 100K shifting the intermolecular contacts. Although there is no low temperature X-ray structural data to support this theory, conductivity data taken on this material shows a jump in the resistance at 120K which is usually indicative of a phase transition in a material of this type [5]. An alternative explanation is that we are observing a two phase phenomenon in the polycrystalline susceptiblity. At high temperatures the response from an antiferromagnetic phase dominates the magnetic susceptibility, whereas below 100K the response from the ferromagnetic phase dominates the observed response. However in all the crystallographic studies performed to this date only one crystal structure has been found for this material.[1,3,6,7]

The mechanism for the ferromagnetic exchange is currently being investigated. We mention in conclusion that we have performed A.C magnetic susceptibility measurements under pressure on this salt to follow the Curie temeperature with changes in lattice constants. The pressure dependence of the Curie Temnperature, T_c, is found to be very large, about 10%/kbar[8]. We note that this is twice the value found for the well known molecular ferromagnet decamethylferrocenium tetracyanoethanide measured by Huang and co-workers.[7] We consider that the sign and size of the exchange in this material is very dependent on the exact nature of the intermolecular contacts within the stacks.

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