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The effect of pressure on the magnetic properties of the molecule-based canted metamagnet decamethylferrocenium 2,3-dicyano-1,4-naphthoquinonide, $FeCp_2^*[DCNQ]$

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Abstract

The pseudo-1D charge-transfer salt decamethylferrocenium 2,3-dicyano-1,4-naphthoquinonide, $FeCp_2^*[DCNQ]$, is an unusual metamagnet that exhibits hysteresis centered on zero applied field in the nominally antiferromagnetically ordered state due to the presence of canting. Measurements of the a.c. susceptibility in a d.c. magnetic field in a He-gas cell up to hydrostatic pressures of 5 kbar have shown an approximately linear increase in both the Néel temperature and the metamagnetic critical field with increasing pressure, consistent with increasing net antiferromagnetic interstack interactions due to decreasing interstack distances.

Keywords: Molecular magnetism; Metamagnetism; Canted antiferromagnetism; a.c. susceptibility; High pressure

1. Introduction

Recently we reported the synthesis, crystal structure and ambient pressure magnetic properties of a metamagnetic air-stable charge-transfer (CT) salt decamethylferrocenium 2,3-dicyano-1,4-naphthoquinonide $FeCp_2^*[DCNQ]$ [1]. Analogous to other one-to-one CT salts built from first-row decamethylmetallocenes and organic one-electron acceptors, such as the structurally similar $FeCp_2^*[TCNE]$ [2], the magnetic state of $FeCp_2^*[DCNQ]$ is believed to be pseudo-1D in nature. As seen in Fig. 1, the compound crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell. As reported previously, the structure consists of mixed 1D stacks of $FeCp_2^*$ cations and DCNQ anions, each with spin $S = 1/2$. There is a small orbital contribution to the moment on the iron. Ferromagnetic interactions along the stacks lead to significant 1D interactions above the Néel temperature ($T_N \approx 4$ K) where 3D antiferromagnetic order sets in.

The most notable property of $FeCp_2^*[DCNQ]$ is its metamagnetism at low temperature, whereby if a sufficiently large magnetic field ($H_c \approx 0.5$ T) is applied, an antiferromagnetic-to-ferromagnetic-like transition occurs, as seen in Fig. 2. Also noteworthy is that in the nominally antiferromagnetic state, the moments are slightly canted such that incomplete cancellation occurs and a weak ferromagnetic (canted antiferromagnetic) state is created. This results in a magnetic hysteresis centered about zero applied field (Fig. 2).

In the present paper we investigate the effect of hydrostatic pressure up to 5 kbar on the two phase observed transitions: (1) from paramagnetic-to-antiferromagnetic order as the temperature is decreased under a small applied a.c. field and (2) from antiferromagnetic-to-ferromagnet-like order as a d.c. field upto 3 tesla is applied at temperatures below T_N. Both the Néel temperature and the critical magnetic field are found to increase significantly with pressure.

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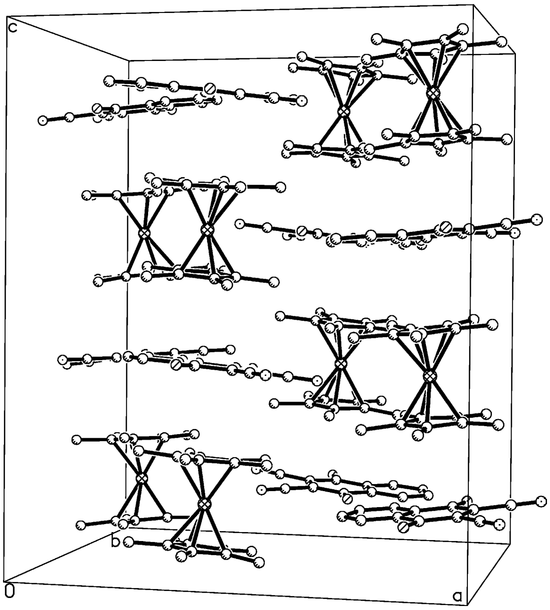

Fig. 1. Unit cell of FeCp$_2^*$[TCNE] illustrating the 1D mixed stack structure.

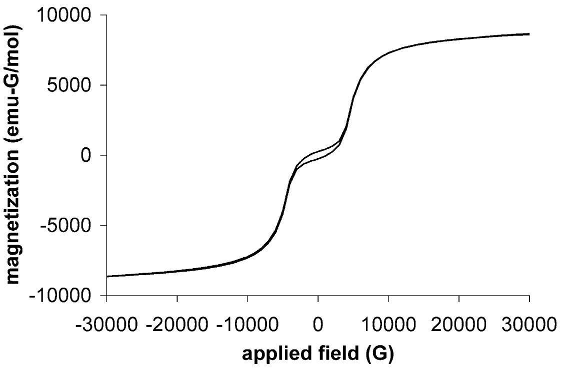

Fig. 2. The d.c. magnetization of FeCp$_2^*$[TCNE] versus applied field at 1.8 K. Note the hysteresis in $M(H)$ at small fields and the metamagnetic transition near 0.5 T.

2. Experimental

The compound FeCp$_2^*$[DCNQ] is formed from the one-pot reaction in dichloromethane of commercially available decamethylferrocene and 2,3-dicyano-1,4-naphthoquinone. Details of the sample preparation and characterization were published previously [1].

The He-gas compressor system (Harwood) used in these experiments is capable of generating hydrostatic pressures up to 14 kbar. The pressure is determined by a calibrated manganin gauge in the compressor system at ambient temperature which remains connected to the CuBe pressure cell (Unipress) through a 3 mm O.D. × 0.3 mm I.D. CuBe capillary tube. The pressure cell is inserted into the variable temperature insert (2–300 K) of a cryostat containing a high-field superconducting magnet to 9 T. The temperature is measured using two pairs of calibrated carbon and platinum thermometers embedded at either end of the pressure cell. Because of the fragility of the molecular crystals, care is taken using a standard procedure [3] to slowly cool through the melting curve of the He pressure medium maintaining a 3 K temperature gradient across the length of the pressure cell so that the He freezes from bottom to top, i.e. towards the capillary tube inlet.

The a.c. susceptibility of the 4.66 mg powder sample of FeCp$_2^*$[DCNQ] in the high pressure environment was measured using a miniature primary/secondary coil system located inside the 7 mm I.D. bore of the pressure cell. A Stanford Research Instruments SR830 digital lock-in amplifier with SR554 preamplifier was employed. The a.c. magnetic field amplitude was 1.0 Oe (rms) at 1023 Hz. Further details of the present experimental setup are given elsewhere [4].

3. Results and discussion

Molecular magnetic solids are particularly well suited for examination under pressure because of their high compressibility and because the magnetic interactions are generally believed to depend strongly on the distance between building blocks, as illustrated by several previous studies [5–8]. The high-pressure study on the molecular magnet most structurally relevant to the present work was carried out by Huang et al. [7] on decamethylferrocenium tetracyanoethenide, FeCp$_2^*$-[TCNE], a CT salt ferromagnet with Curie temperature $T_c \approx 4.8$ K. In their a.c. susceptibility measurements, these workers found T_c to increase with pressure at the rate of $+0.22$ K kbar^{-1} or 4.6% kbar^{-1}. Interestingly, the application of pressure also appeared to induce a structural transition to a phase that exhibited metamagnetism.

We have previously described the structural and magnetic properties of FeCp$_2^*$[DCNQ] as arising from mixed stacks of donors and acceptors exhibiting nearest-neighbor ferromagnetic coupling within the stack as reflected by the positive value of the Curie–Weiss θ [1]. The bulk properties of this solid are then dictated by weaker interstack interactions, probably both ferromagnetic and antiferromagnetic, which give rise to the overall 3D antiferromagnetic order.

In the present experiments the magnetic properties of FeCp$_2^*$[DCNQ] were examined by a.c. susceptibility studies under hydrostatic pressures up to 5 kbar (Fig. 3). The Néel temperature, marking the onset of antiferromagnetic order, is located slightly below a peak in the in-phase component of the a.c. susceptibility, χ', versus T. As reported in [1], the out-of-phase component of the a.c. susceptibility, χ'', shows a weak peak near T_N consistent with the hysteretic behavior seen in Fig. 2 arising from the weak canted antiferromagnetism.

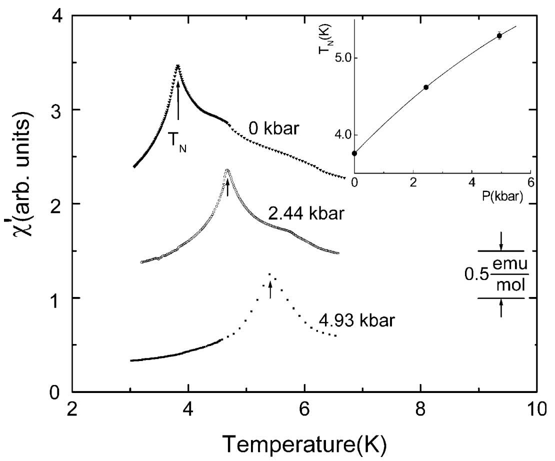

Fig. 3. In-phase component of the a.c. susceptibility at 1.0 Oe (rms) and 1023 Hz versus temperature for $FeCp_2^*[TCNE]$. The vertical position of a given curve is arbitrary; the relative scale is the same for all three curves. The Néel temperature (vertical arrow) is determined as that temperature where $\chi' T$ is maximum. The inset shows T_N versus pressure.

In Fig. 3, the application of pressure shifts the Néel temperature to higher temperatures, indicating an increase in the strength of the net antiferromagnetic interactions. Although there is no generally accepted mechanism for through-space coupling in this class of compounds, we ascribe this to stronger interactions between the stacks, although concomitant stronger intrastack interactions are not precluded. The shift in T_N shows a slight negative curvature with an average slope of approximately $+0.33$ K $kbar^{-1}$ (inset) corresponding to an increase in T_N of 8.7% $kbar^{-1}$, nearly twice the rate of increase of the Curie temperature for $FeCp_2^*[TCNE]$.

In Fig. 4, χ' is plotted as a function of the d.c. bias field to 2 T for two temperatures. At ambient pressure $\chi'(H)$ shows a peak at $H_c \approx 0.8$ T. In the simplest picture, at a given value of the d.c. field H, the a.c. susceptibility would be expected to be proportional to the slope dM/dH of the static magnetization curve $M(H)$ at that field. One would thus expect the maximum in the a.c. susceptibility to occur at that value of the d.c. field where $M(H)$ has maximum slope; from the data in Ref. [1] this appears to occur at $H_c \approx 0.5$ T. The reason for the difference in the determination of the critical field H_c at ambient pressure is not clear.

The data in Fig. 4 indicate that the critical field increases with increasing pressure from ~ 0.8 T at ambient pressure to slightly under 1.6 T at 5 kbar or at a rate of $+0.14$ T $kbar^{-1}$ (inset), corresponding to $\sim +20\%$ $kbar^{-1}$. The pressure-induced increase in the Néel temperature and the critical field for the metamagnetic transition are both consistent with an increase in the net antiferromagnetic coupling between stacks. A similar result was observed by Hosokoshi and co-workers [9] in the pseudo-1D ferrimagnetic chain compound that is constructed from bis(hexafluoroacetylacetonate)manganese(II), $[Mn(hfac)_2]$, bridged by 1,3-bis(*N*-*tert*-butylaminoxyl)benzene.

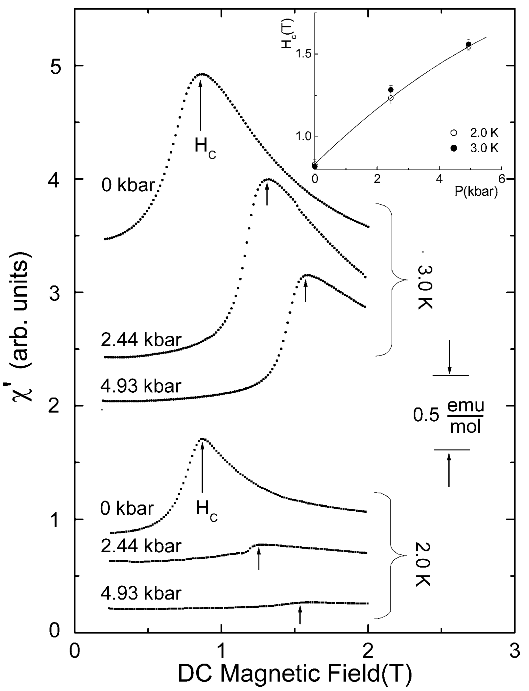

Fig. 4. In-phase component of the a.c. susceptibility χ' of $FeCp_2^*[TCNE]$ versus applied d.c. magnetic field at 2.0 K and 3.0 K for three different pressures. The vertical positions of the curves are arbitrary; the same vertical scale applies to all curves. Vertical arrows mark maxima in $\chi'(H)$ which we identify as critical field for metamagnetism. The inset shows dependence of critical field for metamagnetism on hydrostatic pressure at 2.0 and 3.0 K.

In conclusion, the present studies on the metamagnetic compound $FeCp_2^*[DCNQ]$ show that both the Néel temperature and the critical magnetic field increase significantly under hydrostatic pressure. These results point to an enhancement of the net antiferromagnetic coupling between molecular stacks as these pseudo 1D units are brought closer together under pressure. A quantitative analysis of the present a.c. susceptibility results must await structural studies on this compound under high-pressure conditions.

Acknowledgements

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References

[1] G.T. Yee, M.J. Whitton, R.D. Sommer, C.M. Frommen, W.M. Reiff, Inorg. Chem. 39 (2000) 1874.

[2] (a) J.S. Miller, J.C. Calabrese, H. Rommelmann, S.R. Chittipeddi, J.H. Zhang, W.M. Reiff, A.J. Epstein, J. Am. Chem. Soc. 109 (1987) 769;
(b) J.S. Miller, A.J. Epstein, W.M. Reiff, Science 240 (1988) 40.
[3] J.E. Schirber, Cryogenics 10 (1970) 418.
[4] J.S. Schilling, J. Diederichs, S. Klotz, R. Sieburger, in: R.A. Hein, T.L. Francavilla, D.H. Liebenberg (Eds.), Magnetic Susceptibility of Superconductors and Other Spin Systems, Plenum, New York, 1991, p. 107.
[5] M. Mito, T. Kawae, M. Takumi, K. Nagata, M. Tamura, M. Kinoshita, K. Takeda, Phys. Rev. B. 56 (1997) R14255.
[6] F. Mascarenhas, K. Falk, P. Klavins, J.S. Schilling, Z. Tomkowicz, W. Haase, J. Mag. Mag. Mater. 231 (2001) 172.
[7] Z.J. Huang, F. Chen, Y.T. Ren, C.W. Chu, J.S. Miller, J. Appl. Phys. 73 (1993) 6563.
[8] K. Suzuki, Y. Hosokoshi, K. Inoue, Chem. Lett. 31 (2002) 316.
[9] Y. Hosokoshi, K. Suzuki, K. Inoue, H. Iwamura, Mol. Cryst. Liq. Cryst. 334 (1999) 511.