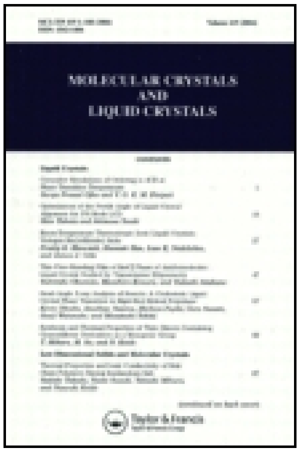

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SPONTANEOUS MAGNETISATION AT 36K IN A SULFUR-NITROGEN RADICAL

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Abstract. The radical p-NCC$_6$F$_4$CNSSN, **1**, can be obtained in two different phases depending upon sublimation conditions. The α-phase, **1**α, crystallises in space group P$\bar{1}$, and the molecules are related through an inversion centre. The β-phase, **1**β, crystallises in the orthorhombic space group Fdd2 and the molecules are not related by an inversion centre. The latter shows a sharp rise in the magnetic susceptibility at 36K which is accompanied by an out-of-phase component in the a.c. susceptibility. Heat capacity measurements show a distinct peak at 35.5K indicative of the long range ordering of the magnetic moments. The magnetic ordering of the compound is also confirmed by neutron diffraction experiments. Magnetisation isotherms indicate the presence of a small residual moment that saturates below 100 Oe. Extrapolation of the residual moment at T= 0K gives a value for the spontaneous magnetisation of 1.5×10^{-3} μ_B/molecule. The behaviour is interpreted in terms of weak ferromagnetism.

INTRODUCTION

The radical p-NC.C$_6$F$_4$.CNSSN, **1**, is a member of a class of heterocyclic dithiadiazolyl radicals, which are usually spin-paired in the solid state through weak inter-molecular S.....S interactions.[1] **1** is the first example of a dithiadiazolyl radical in which this solid state dimerisation is broken. **1** is polymorphic and can be obtained in two different phases depending upon sublimation conditions. The α-phase, **1**α, crystallises in space group P$\bar{1}$, and consists of infinite chains of monomeric radical units packed in a head-to-tail manner and linked through CN...S interactions. Molecules in different chains are related through an inversion centre.[2] The β-phase, **1**β, crystallises in the orthorhombic space group Fdd2 Like **1**α, **1**β consists of infinite chains of monomeric radical units linked through a similar set of CN...S interactions. However the molecules in **1**β are not related by an inversion centre, and the infinite chains are aligned in the same direction whereas those in **1**α are arranged antiparallel to each other.[3]

The magnetic susceptibility of **1**α follows the Curie-Weiss law at high temperatures with θ = -25K and is consistent with a system of unpair S = 1/2 spins. Antiferromagnetic ordering sets in at 8K.[2] The magnetic susceptibility of the β-phase shows a broad maximum centred at 60K and an abrupt increase at 36K.[3] Extrapolation of the inverse susceptibility plot above 120K produces a Weiss constant of θ = -102K indicative of the presence of antiferromagnetic interactions noticeably stronger than those observed for the α-phase. Below 36K the a.c. susceptibility is accompanied by an out-of-phase component indicative of the presence of net magnetic moments in the sample. A very weak residual magnetisation that falls to zero at 36K and saturates as T approaches zero is observed. The results are consistent with weak ferromagnetic behaviour due to a non-collinear antiferromagnetic arrangement of the magnetic moments.[3]

Reports of organic materials exhibiting spontaneous magnetisation are often controversial, particularly when the "ordering temperature" is high and the spontaneous moment is very weak.[4] There is a rather extensive list of substances for which the pretended ferromagnetic-like behaviour turned out to be due to contamination of the sample with small quantities of a ferromagnetic impurity.[4] This paper describes further experiments to investigate the magnetic bahaviour of **1**β, and specifically to confirm the intrinsic character of the magnetic ordering of this compound by means of heat-capacity and neutron diffraction experiments.

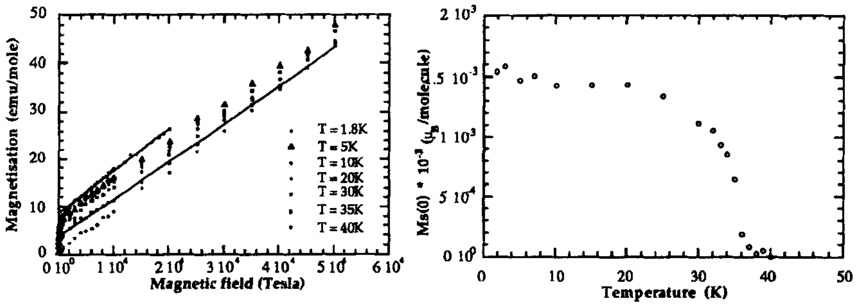
EXPERIMENTAL SECTION

The synthesis of the compound has been described previously.[2, 3] All experiments utilised poly-crystalline samples which were purified by vacuum sublimation. Three sublimations were typically made on each sample in order to remove any non-volatile impurities, such as metal oxides, etc., which might contaminate the sample. The magnetic measurements were made on a Quantum Design SQUID magnetometer equipped with an a.c. susceptibility attachment. Heat-capacity measurements were performed in a commercial a.c. calorimeter for low temperatures (2-300 K) from Sinku-Riko (Model

ACC1-VL). The heat-capacity was determined from the inverse of the sample temperature oscillations induced by the periodic heating at the appropriate frequency. Heat was applied from a mechanically pulsed halogen lampwith an optimum frequency between 1 and 8 Hz depending on the temperature range. The neutron diffraction experiments were performed at the high-flux reactor of the Institut Laue Langevin in Grenoble (France). The sample was placed in a cylindrical vanadium can (d = 5mm, h = 50mm) and inserted into a helium cryostat. The temperature was computer controlled and its stability during the measurements was better than 0.1K. The study of the magnetically ordered phase was made at the high-flux neutron powder diffractometer D1B (λ = 2.52Å). The good resolution at small angles and the high neutron flux make this system very suitable to follow the thermal evolution of the magnetic reflections.

RESULTS AND DISCUSSION

Isothermal magnetisation curves as a function of the magnetic field were made in the temperature range between 1.8 and 40K. The curves are shown in Figure 1a.



(a) (b)

FIGURE 1. a) Magnetisation versus applied field for a series of temperatures. Solid lines are least squares fits to the linear region of the data. b) Zero field extrapolated magnetisation as a function of temperature.

Below 36K the magnetisation of the sample can be interpreted as the contribution of two terms:

$$M(H,T) = M_s(H,T) + \chi(T)*H$$

where $M_s(H,T)$ is the spontaneous magnetisation arising from a ferromagnetic component and χ is the magnetic susceptibility of the sample at the measuring temperature. The $M_s(H,T)$ term saturates at fields below 100 Oe and the curves become linear above some few kOe. The temperature dependence of the spontaneous magnetisationcan be readily determined by extrapolation of these isothermal curves down to $H = 0$. The curve, in Fig. 1b, illustrates the temperature dependence of the spontaneous magnetisation, $M_s(0)$ (μ_B/mole) in the region 1.8 to 40 K. The spontaneous magnetisation tends to $1.5(\pm0.1)\times10^{-3}$ μ_B/mole at 0 K and drops to zero as T approaches 36K. Above 36K the magnetisation of the sample exhibits a linear dependence with the magnetic field, with the gradient equivalent to the sample susceptibility.

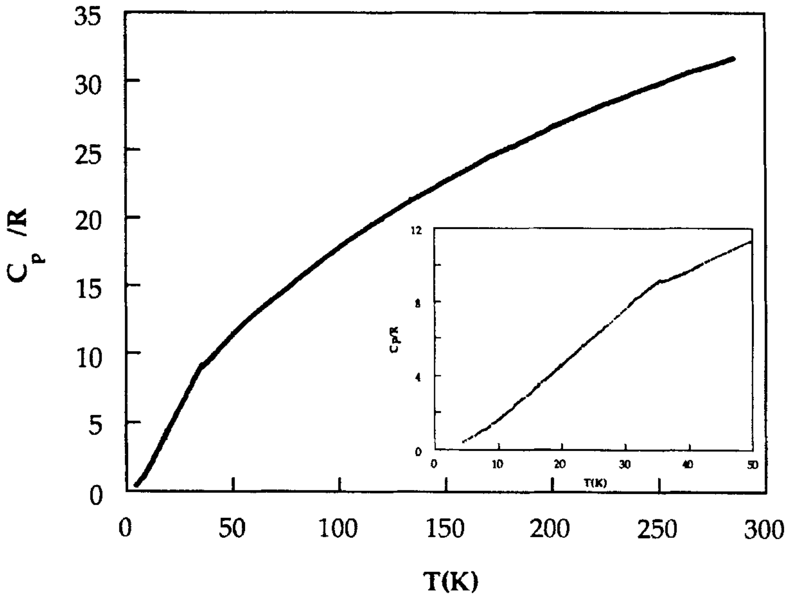


FIGURE 2. Heat-capacity of 1β. The inset magnifies the anomaly observed at 35.5K

A.c. heat-capacity experiments were carried out on a pressed polycrystalline sample (2 x 1 x 0.2 mm) with a weight of around 1 mg. The resulting relative values of the heat-capacity were scaled to absolute values using conventional DSC measurement on a second sample (4.5 mg) in a upper temperature range (250 - 310 K). Absolute accuracy of the DSC data is within ±2 %. The measured heat-capacity is shown in the Figure 2 in absolute units, where the inset corresponds to the low temperature end. A small but clear peak appears at $T_N = 35.5$ K corresponding to the long range ordering of the magnetic moments. This temperature, T_N, agrees well with the susceptibility[3] and magnetisation results. The heat-capacity is composed of at least two terms, of which the lattice and magnetic terms provide the largest contributions. At the magnetic ordering temperature, the lattice contribution is much higher than the magnetic one which accounts for only 3 % of the total value. This makes it difficult to extracted the magnetic contribution from the experimental data.

The broad maximum observed at 60 K in the susceptibility data[3] has been ascribed to short range antiferromagnetic interactions and is indicative of the presence of a certain degree of low dimensionality. A simple estimation based on a linear chains would yield $|J| = 44.2$ K for the intra-chain interaction. This would give a broad heat capacity maximum of 0.35 R value near 40 K. Energetical considerations[5] would give a value for the interchain, J', versus intrachain interaction ratio of about $|J'/J| = 0.5$. Such a ratio value indicates that the propagation of magnetic interactions in the system has a rather strong three dimensional character, and as such, these values for the exchange interactions should only be considered as upper and lower limits.

A structural requirement for weak ferromagnets is that the magnetic and nuclear lattices must be equal, since the lack of collinearity of the spins must not change the magnetic symmetry of the crystal.[6-8] This is confirmed by neutron diffraction experiments. Diffraction patterns were measured at 1.5 K, where the sublattice magnetisation should be practically saturated, and at 50K, a temperature which is well into the paramagnetic regime although not far from T_N. This choice of temperatures, imposed by the magnetic characteristics of the sample, produces a rather large temperature difference for the two data sets and the effects of lattice contraction produces noticeable shifts in the positions of the Bragg reflections. Since the magnetic moment (S = 1/2) is partially delocalized in the molecule,[1] the intensities of the magnetic Bragg reflections were expected to be very weak. Consequently, a counting time of three hours was set for each diffraction pattern. Although this time was not enough to obtain good statistics, it was suficient to allow differences between the paramagnetic and the antiferromagnetic regimes to be observed. A difference diagram (Figure 3) where the nuclear contribution (pattern at 50K) has been substracted from the nuclear and magnetic one (pattern at 1.5K), emphasises the magnetic contributions arising in the magnetic Bragg reflections (111) and (220). The negative peaks correspond to the (substracted) nuclear reflections. The nuclear lattice contraction observed on cooling tend to move the peak positions toward larger θ angles. Nevertheless, the difference in the (220) reflection between the negative and the positive peaks gives a net positive contribution that corresponds to the magnetic reflection. The situation is different in the case of the (311) reflection, where the negative and the positive peaks seem to be equal and no magnetic contribution can be observed. Figure 3 also illustrates that no extra reflections are present in the low temperature diffraction pattern. This is indicative of a propagation vector **k** = 0 and is in good agreement with the non colinear character of the magnetic structure.

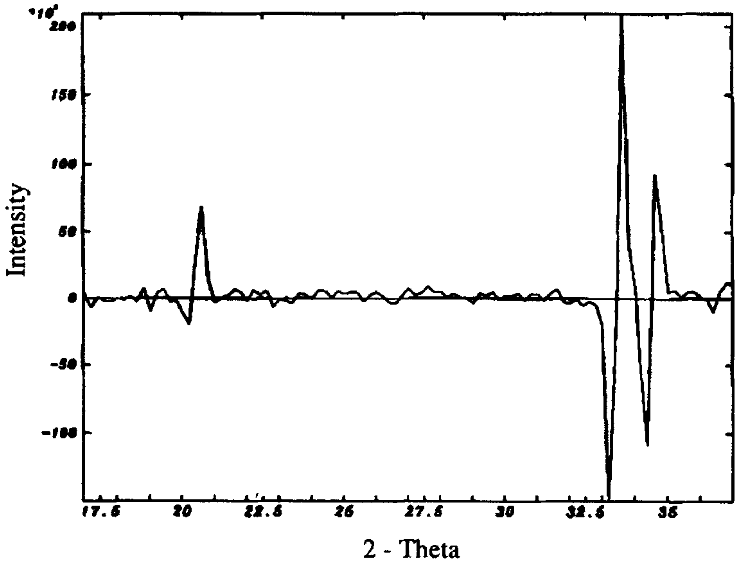


FIGURE 3. Difference diagram of 1β between powder diffraction patterns measured at 1.5 K (nuclear and magnetic lattice) and 50 K (nuclear lattice).

Magnetic and heat-capacity measurements reported here clearly indicate that the sample undergoes a magnetic phase transition at 35.5K from a paramagnetic state into a magnetically ordered one. The neutron diffraction experiments are also indicative of magnetic structure at low temperature. The magnetisation measurements are consistent with weak ferromagnetism. Since the structure is non-centrosymmetric, canting may arise through a Dzyaloshinsky-Moriya (DM) interaction, which minimises the coupling energy tending to rotate the moments away from collinearity.[6, 8] The strength of the DM interaction is proportional to the spin anisotropy, $\Delta g/g$, which for **1β** is found to be 0.005±0.001 from e.p.r. measurements. Such a small value of the spin anisotropy is suficient to slighty rotate the moments away from antiparallel alignment (the canting angle, estimated from the magnitud of the spontaneous magnetic moment, $M_s(0)$, is 0.085°. This is a very unusual spin árrangement for a purely organic compound. To the best of our knowledge two triphenylverdazyl derivatives are the only other well established examples where spin canting due to DM interactions have been found thus far.[9, 10] In addition, the ordering temperature at which the molecule exhibits a spontaneous magnetic moment, is the highest yet reported for any open-shell organic molecule.

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