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Abstract. We present magnetic studies of a pure organic compound, which shows signs of antiferrogmagnetic order at 1.35 K. The magnetic ordering temperature is comparable to the Curie–Weiss temperatures from both AC and DC susceptibility results. In low-temperature magnetization, there appear two distinct features: a low-field spin-flop transition and an abrupt saturation of magnetization at 5.7 T.

1. Introduction

With interest increasing in organic-based compounds, growing numbers of pure organic compounds are found to have magnetic ground states at low temperatures [1]. While most magnetic organic compounds have an antiferromagnetic character [2], there are also a few examples of organic compounds with ferromagnetic order [3]. Over the past few years, many new compounds have been added to this interesting magnetically ordered organic group, and phenomenological models have been put forward for magnetic order in the organic compounds [1]. Inevitably, however, the present studies of magnetism in organic compounds focus on how the magnetic ground state of organic compounds behaves under different structural and chemical configurations.

One interesting aspect of magnetic order in organic compounds is that it is due to s and p electrons. It is conceivable that well localized s and p electrons in the organic compounds behave like d and f electrons in metals; so we can use concepts developed in the studies of metallic magnetism to understand the magnetic properties of the magnetic organic compounds. We may, however, also need quite different approaches here. It is interesting that magnetic organic compounds often have a quasi-one-dimensional (quasi-1D) structure. One can thus compare experimental results more closely with thoroughly studied theoretical models on the magnetic properties of a one-dimensional (1D) system, which is almost impossible in metallic magnetism.

In the paper, we present magnetic properties of a pure organic compound, p-nitrophenyl nitronyl nitroxide (NIT3Py), '$C_{12}H_{16}N_3O_2$' In the discussion, we shall discuss our data in the light of a modified 1D Heisenberg model [4, 5].

2. Experimental details

The NIT3Py crystallizes in a structure of orthorhombic symmetry with the space group $P2_12_12_1$. We used a homemade AC susceptometer and two SQUID magnetometers. The AC susceptometer operates at 119 Hz and with a 2 Oe driving magnetic field down to 1.5 K. A SQUID magnetometer was used for DC susceptibility measurements from 300 to 5 K. For magnetic studies at low temperatures, we utilized a second SQUID magnetometer developed at CRTBT, CNRS, Grenoble, which is equipped with an 8 T superconducting magnet and a dilution refrigerator capable of reaching 100 mK. To measure AC susceptibility, we used a 33.5 mg sample encapsulated in plastic. For the low-temperature SQUID magnetometer, however, we wrapped 94.5 mg of the sample in between two foils made of copper wire using PTFE tape, which were thermally anchored to the mixing chamber.
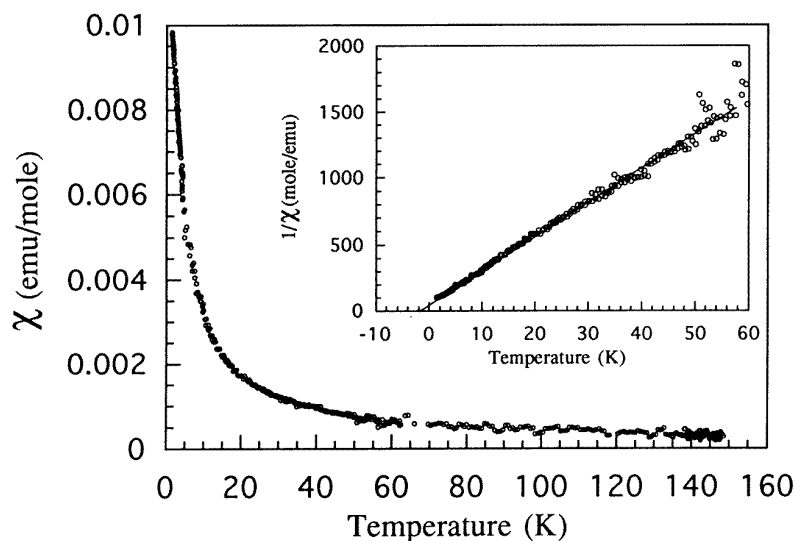

Figure 1. AC susceptibility displayed as a function of temperature. The inset shows the inverse susceptibility with the Curie–Weiss temperature at around −2 K.

3. Results and analysis

In figure 1, we present the AC susceptibility and the inverse AC susceptibility. In the inverse susceptibility, there is a good Curie–Weiss behaviour from 60 to 3 K with a small negative intercept (about −2 K). The effective magnetic moment μ_{eff} is estimated to be around $0.557\mu_B$. Since the Curie–Weiss temperature Θ_{CW} is small and negative, the organic compound NIT3Py is expected to have weak antiferromagnetic interactions. Although the AC susceptibility does not show any sign of magnetic order down to 1.5 K, it is noticeable that the AC susceptibility tends to saturate below 2 K. This tendency to saturation at low temperatures seems to be in good agreement with the weak antiferromagnetic interactions, inferred from the small negative Curie–Weiss temperature.

Using the two SQUID magnetometers, we also measured the DC susceptibility from 300 to 5 K with 0.5 T and from 2.5 to 0.17 K with 0.1 T (figure 2). One distinct feature in the DC susceptibility is the peak appearing at 1.35 K. Since it is rather sharp
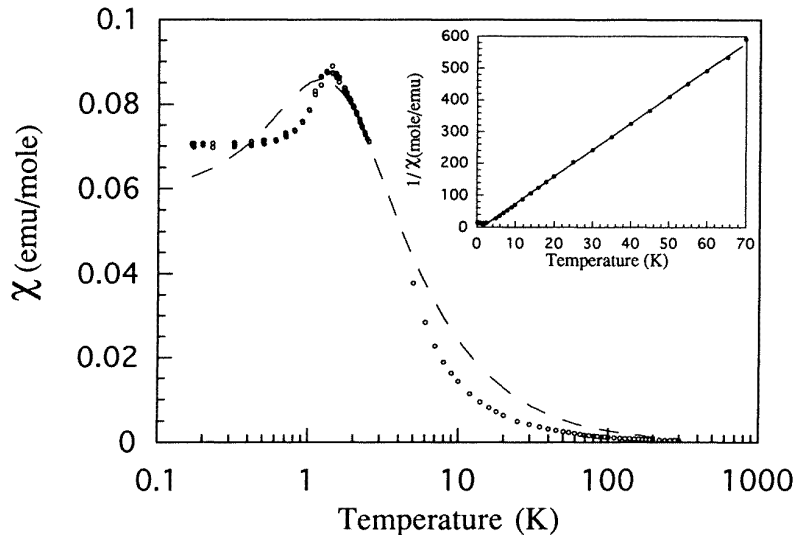
Figure 2. Semilogarithmic plot of DC susceptibility. The line is the result of curve fitting using a susceptibility formula from the 1D Heisenberg model with $J/k_B = 0.93$ K (see the text). The inset shows the inverse susceptibility with the Curie–Weiss temperature at around 2 K.

and its transition temperature is comparable to the Curie–Weiss temperature, we believe that it indicates antiferromagnetic order, more than just the development of short-range mangetic fluctuations. This view is strengthened further by magnetization studies. Unlike the AC susceptibility results, the DC susceptibility shows a small positive Curie–Weiss temperature (about 2 K), indicating the presence of ferromagnetic interactions at slightly elevated magnetic fields. Regarding this, we would like to recall that the AC susceptibility results were taken with a 2 Oe magnetic field, and the high-temperature DC susceptibility with a 0.5 T magnetic field. With respect to the different magnetic fields used in the two measurements, it is interesting to note the observation of a weak transition at around 0.3 T in a magnetization versus field curve at low temperatures, which will be discussed shortly.

To study further the antiferromagnetic ground state, we measured magnetization at low temperatures up to 8 T (figure 3). In the magnetization curve taken at 180 mK, one can observe two interesting features. One is a weak transition at around 0.3 T. It is clearly shown in the inset to figure 3 and disappears upon increasing the temperature above 1 K. To demonstrate better how the weak transition evolves with temperature we present two other magnetization cuves taken at 1 and 4.2 K in the inset as well. For the sake of presentation, we moved the 0.18 and 1 K data upwards by 200 emu mol^{-1} each. A line is drawn from the data between 0.4 and 1 T to illustrate the non-linearity of magnetization at 0.18 K. As the temperature increases, the non-linearity becomes weaker at 1 K and disappears at 4.2 K altogether. That the weak transition disappears on increasing the temperature above 1 K coincides with the antiferromagnetic transition at 1.35 K.

Above the 0.3 T transition, the magnetization shows a slight indication of saturation before undergoing an abrupt change at around 5.7 T and becoming saturated. The saturated magnetic moment value μ_{sat} is around $0.82\mu_B$ FU. The difference between μ_{eff} ($= 0.557\mu_B$) from the AC susceptibility measurements and μ_{sat} ($= 0.82\mu_B$) from the magnetization data, we think, is likely to be due to a field-induced moment. Within the experimental error, we
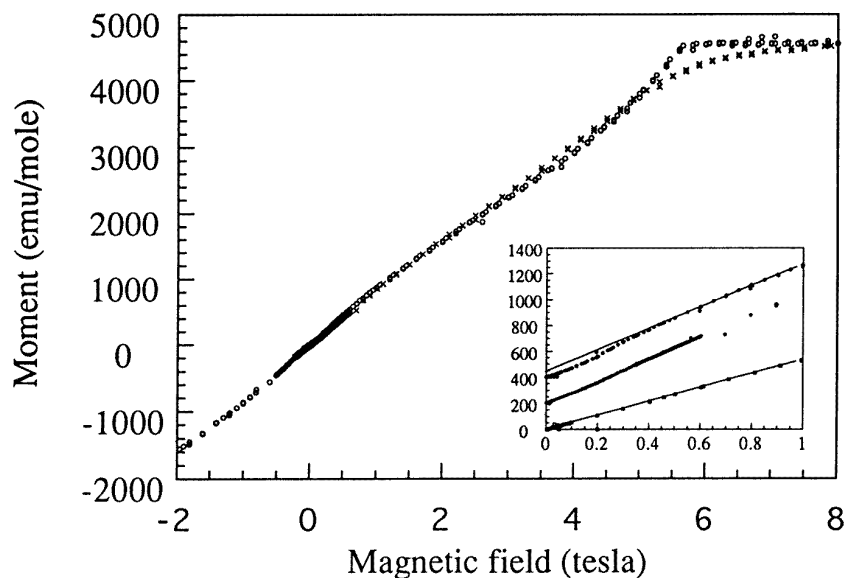
Figure 3. Magnetization versus magnetic field at 0.18 K (○) and 1 K (×). The inset is a magnified picture of magnetization in the low-field region, taken at 0.18, 1 and 4.2 K (from top to bottom). For better presentation, data for 0.18 and 1 K have been displaced upwards by 200 emu mol^{-1} each. Lines are linear extrapolations from data between 0.4 and 1 T (5583 emu mol^{-1} corresponds to $1\mu_B$/FU).

cannot observe a hysteresis in the magnetization.

That we have seen two different Curie–Weiss temperatures in the AC and DC susceptibilities may well be due to the difference between the magnetic states below and above 0.3 T, which is indicated by the 0.3 T transition. However, the change at 0.3 T is rather small.

Concerning the overall behaviour, it is interesting to note that the high-field magnetization does not have a downward curvature typical of the Brillouin function. The absence of downward curvature and the abrupt saturation of magnetization, in particular, seems to resemble certain aspects of the results of the 1D Heisenberg model. Indeed, the quasi-1D structure of NIT3Py may not be irrelevant in this matter. To consider this futher, we compared the normalized magnetization at 180 mK with theoretical calculations given in [4] with $J/k_B = 1.9$ K. Although there are limited similarities at high fields, especially the abrupt saturation, the general agreement between theory and experiment is far from satisfactory. We also tried to fit the experimental DC susceptibility using a susceptibility formula with $J/k_B = 0.93$ K for the 1D Heisenberg model, given in [6] (see figure 2). Although overal agreement is better in susceptibility than in magnetization, the 1D Heisenberg model is not capable of fully reproducing the detailed structure of the DC susceptibilty either. Including inter-chain interaction in the calculations does not improve the agreement much.

On balance, the organic compound NIT3Py seems to have certain characters of the 1D Heisenberg model, but full understanding of the magnetic properties of NIT3Py needs to be dealt with beyond the 1D Heisenberg model; indeed, there is no phase transition in a strictly 1D model.

4. Discussion

In the discussion, we would like to comment on the weak transition seen in the magnetization at around 0.3 T at 0.18 K. Regarding this, two observations deserve particular attention. First, it is a relatively modest transition, and a much more abrupt transition appears at higher magnetic fields. Secondly, an extrapolation between 0.4 and 1 T does not lead to $M = 0$ at $H = 0$ in the 180 mK data. In fact, the extrapolation of data from 0.4 and 1 T has a slope of 838 emu mol^{-1} T^{-1} ($\simeq 0.15\mu_B$ T^{-1}) and an intercept of 32.5 emu mol^{-1} ($\simeq 0.005\,82\mu_B$). Since it is a rather weak transition and there is a linear H region in the magnetization above the critical field, it is likely to be due to a spin-flop transition, i.e. the rotation of the antiferromagnetic axis with increasing magnetic field. To understand the non-zero extrapolation of the magnetization at $H = 0$, we feel that we have to go beyond a standard Heisenberg Hamiltonian. For analysis, we propose a toy model with a weak Dzyaloshinsky–Moriya term

$$J'\boldsymbol{S}_i \times \boldsymbol{S}_j$$

a Heisenberg exchange term

$$J\boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

and a Zeeman term

$$\boldsymbol{M} \cdot \boldsymbol{H}$$

for the magnetization above the weak spin-flop transition. Using the model within the mean-field approximations, we can take the derivative of the total energy with respect to an angle between moments and field under the assumption of a non-collinear spin structure above the spin-flop transition. This analysis leads to a spin-flop transition with a slope of

$$\frac{M_{sat}^2}{4J}$$

and an intercept of

$$\frac{M_{sat}J'}{2J}.$$

If we substitute the effective moment value, $0.557\mu_B$, for M_{sat}, then we shall have $J = 0.347$ K and $J' = 0.0073$ K. These J- and J'-values seem to be reasonable and in particular, the J-value for the Heisenberg exchange term agrees with J-values estimated from the magnetization and susceptibility analysis using the 1D Heisenberg model.

In conclusion, we have observed an antiferromagnetic transition at 1.35 K in a pure organic compound $C_{12}H_{16}N_3O_2$. The magnetization displays two distinct features: one is the low-field spin-flop transition and the other the abrupt saturation of magnetization at much higher magnetic fields. Using simple model calculations, we have shown that the Dzyaloshinsky–Moriya term included in the usual Heisenberg Hamiltonian might be useful for the proper analysis of the low-field magnetization of NIT3Py.

References

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