

SINGLE CRYSTAL MAGNETIC STUDY ON
FERROMAGNETIC MANGANESE(II) PHTHALOCYANINE

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ABSTRACT

A magnetic study has been carried out in the temperature range 1.2 - 25 K and magnetic field range 0 to 50 kOe on single crystals of manganese(II) phthalocyanine. At higher temperatures the magnetic properties of manganese(II) phthalocyanine exhibit chain-like characteristics which may be understood in terms of ferromagnetic Heisenberg intrachain exchange of $S = 3/2$ ions with a weak antiferromagnetic inter-chain interaction. In the ordered state, $T_c = 8.3$ K, MnPc is a canted ferromagnet with easy axes of magnetization being along x_1 and x_3 directions. A zero-field splitting of the single ion 4A_2 state of the manganese(II) ion gives rise to canted ferromagnetism which does not show complete saturation at the high field range of these experiments (50 kOe). The spin structure of manganese(II) phthalocyanine at low temperature is discussed.

INTRODUCTION

Manganese(II) phthalocyanine (MnPc) is a planar molecule and is known to be isostructural to other divalent metal phthalocyanines.^{2,3} The stacking of the planar MnPc molecules in the crystal lattice is shown in Figure 1. The figure shows that the two pyrrole nitrogen atoms of each molecule lie exactly above or below the Mn atom belonging to nearest neighbours. The distance between these axially located nitrogen atoms and the Mn atom is 3.4 Å and thus may provide a possible pathway for magnetic exchange interactions. The Mn(II) ions lie on linear arrays parallel to the b-axis of the molecule such that MnPc may be considered as containing magnetic linear chains along the b-axis of the crystal.

Magnetic susceptibility and magnetization measurements on MnPc down to 1.4 K have established that the Mn(II) ion in MnPc is in a $S = 3/2$ spin state, and that MnPc behaves as a molecular ferromagnet at low temperatures.⁴ A qualitative explanation for the ferromagnetism was given in terms of the overlap of d-orbitals of the Mn(II) ion and the π -system of the phthalocyanine ring.⁴ The data were later quantitatively explained in terms of a model for $S = 3/2$ linear chain exhibiting ferromagnetic interactions, and a value for the exchange energy of $J = + 7.6 \text{ cm}^{-1}$ was deduced.⁵ Existence of ferromagnetism in MnPc was subsequently confirmed by Miyoshi et al,^{6,7} who also determined the Curie temperature to be 8.6 K.

To determine easy axis of magnetization in MnPc, Miyoshi⁸

measured the single crystal magnetization at 4.2 K. MnPc belongs to monoclinic system with two crystallographically inequivalent molecules in the unit cell, and crystals generally grow as long flat needles elongated along the b-axis. Crystals used by Miyoshi were very small weighing less than 10^{-2} mg. The 'single crystal' magnetization measurements were therefore made on a bundle of single crystals oriented along the long b-axis of the crystals. Miyoshi measured magnetization along and perpendicular to this long axis (i.e. b-axis) of this bundle, and concluded that easy axis of magnetization lies along the b-axis of the crystals.

Our magnetic anisotropy measurements on individual single crystals of MnPc in the temperature ranges 80-300 K⁴ and 20-100 K⁹ have revealed that the (ac) plane of the MnPc crystal is highly anisotropic. In the above measurements of Miyoshi, the anisotropy in the (ac) plane was averaged to zero because of the random orientation of the crystallites. Thus, conclusions derived from the measurements were subject to ambiguities.

An accurate magnetic measurement on a single crystal of MnPc at low temperatures therefore was desirable in order to determine the spin structure in the ferromagnetic region. The present paper describes results of magnetization measurements in the 2-15 K temperature range on large, well-developed individual single crystals of MnPc.

TECHNIQUES

Single crystals of MnPc were grown by a vacuum sublimation technique. The monoclinic crystals grow as long, thick plates with well developed (001) faces. The crystals used in the present measurements weighed between 4-7 mg.

Single crystal susceptibilities were measured with a vibrating sample magnetometer.¹⁰ In a monoclinic crystal one of the three principal susceptibilities, say χ_3 , lies along the b-axis of the crystal, with the other two, χ_1 and χ_2 , being in the (ac) plane at some angle to the a- and c-axis. This angle must be determined by experiment. In this work the orientation of χ_1 and χ_2 were determined, and χ_1 , χ_2 and χ_3 were determined as function of temperature and external magnetic field.

A single crystal of MnPc weighing about 5 mg was mounted on a Lucite goniometer head of the VSM probe with the b-axis vertical so that the (ac) plane containing χ_1 and χ_2 was lying in the horizontal magnetic field. The temperature was held constant at 4.2 K. The crystal was then rotated through the graduated goniometer head, and the moment (or susceptibility) was measured at an interval of every 10°. A plot of the angular dependence of the moment is shown in Figure 2. It is apparent that the maximum moment direction (say χ_1) lies at ca 20° from the a-axis of the crystal. The relative orientation of the three principal susceptibilities at 4.2 K is shown in Figure 3. Magnetization along these susceptibility directions was easily measured with varying field and temperature by setting these

crystal directions along the magnetic field. The magnetization up to 50 kOe along the long b -axis (χ_3 direction) was also measured with a second VSM assembly equipped with a superconducting magnet.

RESULTS

The temperature dependencies of the average (2-25 K) and principal susceptibilities between 4-15 K are shown in Figures 4 and 5. The measurements were done at a magnetic field of 30 Oe for $\bar{\chi}$ and at 50 Oe for the principal susceptibilities, χ_i ($i = 1, 2, 3$). The data at lower magnetic fields become slightly less accurate particularly for the single crystals above 10 K or so, but the data show similar temperature dependencies. The $\bar{\chi}$, as expected, shown an abrupt large increase below 9 K, and the magnitude of $\bar{\chi}$ does not maximize even at the lowest temperature of the measurements, ca 2 K. The Curie temperature was obtained from the point of inflection in the χ vs T plot. We obtained $T_C = 8.3$ K, in good agreement with the value of $T_C = 8.6$ K obtained previously from broadline NMR studies. The temperature dependence of the principal susceptibilities shown a large anisotropy in (χ_1, χ_2) with χ_1 increasing very rapidly below 8 K. $\chi_3 (= \chi_b)$ and particularly χ_2 are relatively much smaller in magnitude and show much less variation with temperature. The results of Figure 5 clearly establish that χ_1 is the direction of the easy axis of spin alignment. For a molecular ferromagnet χ_1 should have been independent of the temperature below T_C ;^{11,12} however MnPc does not show such behavior down to 4 K.

We measured χ_1 therefore below 4 K and observed that at ca 2 K χ_1 becomes almost independent of temperature (Figure 6). Further, a small but reproducible kink is observed in the χ_1 vs T plot at 3.5 K. A possible explanation of these observations is that a small but finite antiferromagnetic exchange interaction exists between the chains, in addition to the apparently dominant ferromagnetic intra-chain interaction. Above 3.5 K this ferromagnetism dominates the weak inter-chain antiferromagnetic interaction, with the kink in the χ_1 vs T curve presumably representing this latter interaction.

Figure 7 summarizes the single crystal magnetization data at 4.2 K along χ_1 (σ_1), χ_2 (σ_2) and χ_3 (σ_3) directions, as well as the average magnetization ($\bar{\sigma}$) of a powdered sample. Several features of the results are noteworthy. First, the data confirm that χ_1 is an easy axis of magnetization though the sample can be magnetized nearly as easily along χ_3 as well. Further the large anisotropy and difference in magnetization behavior between σ_1 and σ_2 is consistent with their corresponding temperature dependencies. The most significant result is that although σ_1 reaches a near saturation value even at a magnetic field at ca 3 kOe, complete saturation is not reached up to a magnetic field of 15 kOe. The same behavior obtains for σ_2 and σ_3 . In fact, σ_3 does not reach complete saturation at 4.2 K in a magnetic field of 50 kOe (Figure 8).

DISCUSSION

First, we compare our results with those of Miyoshi.^{6,7} There are significant differences in the magnetization data. Our

magnetization data (as well as χ_i vs T data) show that the σ_1 direction is most easily magnetized. The reason for the discrepancy between our work on a single crystal and the earlier work^{6,7} may be understood in terms of the anisotropy of the material. We find that the magnetization in the (ac) plane of MnPc, which contains σ_1 and σ_2 , is extremely anisotropic. In the earlier work measurements were made on a bundle of crystals which were randomly oriented in the (ac) plane, with measurements being made parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the bundle axis (i.e., the b-axis). The σ_{\parallel} from the earlier work^{6,7} corresponds to our σ_3 , and the σ_{\perp} corresponds to some average of our σ_1 and σ_2 . Since σ_1 and σ_2 are very different in magnitude, the experimentally observed average, that is σ_{\perp} , came out to be smaller than σ_1 , and consequently, an erroneous conclusion concerning the easy direction was arrived at. The value for σ_1 from the earlier work^{6,7} is in reasonable agreement with our σ_3 ; at 4.2 K we obtained a value of 12×10^3 emu for σ_3 , while Miyoshi obtained a value of 14×10^3 for σ_1 at the same temperature. The discrepancy arises from the relatively large uncertainties inherent in the measurements on the bundle of MnPc crystals.

The fact that the magnetization of the MnPc increases linearly with the magnetic field at higher fields and does not show complete saturation even up to 50 kOe is indicative of a canted ferromagnetic spin structure. The canted moments are

assumed to rotate gradually with increasing magnetic field in a single domain region. Using the formula $\sigma = \sigma_0 + \chi H$, the spontaneous magnetization σ_0 can be obtained from Figure 7. For powdered and single crystal samples, the values are: $\sigma_0^{AV} = 12.5$ emu/g and $\sigma_0 \chi_1 = 21.4$ emu/g. Since σ_0^{AV} is the spatial average, $\sigma_0^{AV} = 0.57 \sigma_0 \chi_1$. Taking the above value for $\sigma_0 \chi_1$ we calculate $\sigma_0^{AV} = 12.2$ emu/g in good agreement with the observed value.

$\sigma_0 \chi_1$ corresponds to the moment $\langle \mu \rangle = 2.17 \mu_B/\text{ion}$ which is less than $3.0 \mu_B/\text{ion}$ expected for an $S = 3/2$ spin state of MnPc. If the magnetic moments are assumed to align along their tetragonal axes making the angle between them nearly 90° , the resultant ferromagnetic moment will be $2.12 \mu_B/\text{ion}$ in agreement with the observation.

We now discuss the spin structure of MnPc at low temperatures. We have mentioned earlier that MnPc has two crystallographically inequivalent magnetic sites with each site constituting a magnetic chain. The magnetic moments within the chain interact ferromagnetically (J positive).⁵ There appears to be a feeble inter-chain interaction (J') and the results shown in Figure 5 suggest that it is antiferromagnetic. Above about 3 K the intrachain ferromagnetic interaction overtakes this inter-chain interaction. The magnetic properties of MnPc can then be discussed using the Hamiltonian:^{6,7}

$$\mathcal{H} = -2 \sum_{ij} J \hat{S}_i \cdot \hat{S}_j - 2 \sum_{jk} J' \hat{S}_j \cdot \hat{S}_k + \sum_j D (\hat{S}_j^x)^2 + \sum_k D (\hat{S}_k^y)^2$$

The first and second terms are exchange interactions in and between the chains, respectively and the experimental results

show that J is positive and J' is negative. The third and fourth terms are the single ion anisotropies at the two sites, D being the zero-field splitting parameter of the ground 4A_2 state of the $S = 3/2$ manganese(II) ion in MnPc. At 4.2 K the relative orientation and magnitude (i.e. $\chi_1 > \chi_2$) of the principal susceptibilities suggest, on the basis of crystal field theory,⁵ that D is negative. Miyoshi has discussed the spin structure of MnPc on a two sublattice model and shown that for both J' and D negative, the spins are perpendicular to χ_2 axis. As a result the spins on the two sublattices are not antiparallel to each other, and the residual moment gives rise to canted ferromagnetism. Hence the negative D is responsible for the canted ferromagnetism in MnPc, with both χ_1 and χ_3 directions being easy magnetization directions (see Figure 7). This canting of spins causes the magnetic moment to rotate in an external magnetic field, and the magnetization does not show complete saturation even at very high fields. For $g=2$ the resulting magnetic moment is given by

$$\mu = 8B \left[\left(1 + \sqrt{A^2/(A^2+4)} \right)^{1/2} \pm \left(1 - \sqrt{A^2/(A^2+4)} \right)^{1/2} \right]$$

where $A = D/4J'$. For J' negative the magnetic moment varies from 0 to $2.1 \mu_B$. Since $|D| \gg |J'|$, a limiting value for the moment of $2.1 \mu_B$ is predicted, a value which is in good agreement with the experimentally observed magnetic moment.

In this case the magnetic moments are aligned nearly along

their tetragonal axes. As shown in Figure 9, this alignment of magnetic moments gives rise to four kinds of spin structures at low temperatures. It may be seen that the resulting moments lie along x_1 or x_3 directions.

CONCLUDING REMARKS

The ferromagnetism observed in MnPc is rather unique among metal phthalocyanines. For example, even among isostructural analogues, CoPc shows only feeble antiferromagnetism while CuPc behaves as a normal paramagnet down to 1 K.^{4,6} The ground state of FePc is effectively nonmagnetic, and there is no evidence of magnetic ordering down to 1 K. The ferromagnetism in MnPc can be understood, at least qualitatively, in terms of the electronic configuration and the 90° superexchange mechanism, (the Mn-N-Mn angle is nearly 90°). The d -electron configuration of the Mn^{2+} ion in MnPc is $(b_{2g})^2 (e_g)^2 (a_{1g})^1$. It has been shown⁴ that the overlap of e_g and a_{1g} orbitals containing unpaired d -electrons with phthalocyanine molecular orbitals of A_{2u} , E_g , B_{2u} and B_{1u} symmetry will lead to ferromagnetism, as indeed is observed in MnPc.⁴

The spins in MnPc are appreciably canted, arising from the substantially large zero-field splitting of the 4A_2 ground state of the Mn^{2+} ion. An earlier crystal field calculation,⁵ based on the high temperature (80-300 K) single crystal susceptibility data, has shown that the splitting is about 40 cm^{-1} in MnPc and that ${}^4A_2 (\pm 1/2)$ lies below ${}^4A_2 (\pm 3/2)$ state. It is however of interest to note that the directions of x_1 and x_2 have

interchanged in the ordered state with respect to the high temperature directions, giving rise to negative zero-field splitting (i.e. ${}^4A_2 (\pm 3/2)$ lying below ${}^4A_2 (\pm 1/2)$). It is this large negative zero-field splitting which is responsible for the canted ferromagnetism. Thus, the unusual, magnetic behavior of MnPc appears to derive from a combination of magnetic interactions, the electronic configuration of the manganese ion, the low symmetry structure of the compound, and crystal field effects.

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FIGURE CAPTIONS

- Figure 1. The stacking arrangement of planar manganese(II) phthalocyanine molecules along the crystallographic b-axis.
- Figure 2. The angular dependence of the moment as a function of crystal orientation at 4.2 K. In these measurements, rotations were made about the b axis, which was perpendicular to the magnetic field. It may be seen that the principal direction designated χ_1 , is rotated 20° from the a axis.
- Figure 3. The relative orientation of the three principal magnetic susceptibilities of manganese(II) phthalocyanine at 4.2 K.
- Figure 4. The temperature dependence of the average magnetic susceptibility of manganese(II) phthalocyanine in the temperature range 2 - 25 K.
- Figure 5. The temperature dependence of the principal magnetic susceptibilities of manganese(II) phthalocyanine in the temperature range 4 - 16 K.
- Figure 6. The temperature dependence of χ_1 which shows a kink in the χ_1 versus T curve at ~ 3 K and the temperature independence of χ_1 below 2 K.
- Figure 7. Single crystal magnetization data at 4.2 K along χ_1 (σ_1), χ_2 (σ_2), and χ_3 (σ_3) directions.

Figure 8. Single crystal magnetization data for manganese(II) phthalocyanine at 4.2 K in magnetic fields up to 50 kOe.

Figure 9. The four kinds of spin structures in manganese(II) phthalocyanine at low temperatures. The resultant moments are seen to lie along χ_1 and χ_3 . T_1 and T_2 represent the two sites for the tetragonal MnPc molecules.

b-axis

















