

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.<sup>2,3</sup> 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.<sup>4</sup> A qualitative explanation for the ferromagnetism was given in terms of the overlap of d-orbitals of the Mn(II) ion and the  $\pi$ -system of the phthalocyanine ring.<sup>4</sup> 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.<sup>5</sup> Existence of ferromagnetism in MnPc was subsequently confirmed by Miyoshi et al,<sup>6,7</sup> who also determined the Curie temperature to be 8.6 K.

To determine easy axis of magnetization in MnPc, Miyoshi<sup>8</sup>

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 K<sup>4</sup> and 20-100 K<sup>9</sup> 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.<sup>10</sup> In a monoclinic crystal one of the three principal susceptibilities, say  $\chi_3$ , lies along the b-axis of the crystal, with the other two,  $\chi_1$  and  $\chi_2$ , 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  $\chi_1$  and  $\chi_2$  were determined, and  $\chi_1$ ,  $\chi_2$  and  $\chi_3$  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  $\chi_1$  and  $\chi_2$  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  $\chi_1$ ) 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 ( $\chi_3$  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,  $\chi_i$  ( $i = 1, 2, 3$ ). 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  $\chi$  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 ( $\chi_1, \chi_2$ ) with  $\chi_1$  increasing very rapidly below 8 K.  $\chi_3 (= \chi_b)$  and particularly  $\chi_2$  are relatively much smaller in magnitude and show much less variation with temperature. The results of Figure 5 clearly establish that  $\chi_1$  is the direction of the easy axis of spin alignment. For a molecular ferromagnet  $\chi_1$  should have been independent of the temperature below  $T_C$ ;<sup>11,12</sup> however MnPc does not show such behavior down to 4 K.

We measured  $\chi_1$  therefore below 4 K and observed that at ca 2 K  $\chi_1$  becomes almost independent of temperature (Figure 6). Further, a small but reproducible kink is observed in the  $\chi_1$  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  $\chi_1$  vs T curve presumably representing this latter interaction.

Figure 7 summarizes the single crystal magnetization data at 4.2 K along  $\chi_1$  ( $\sigma_1$ ),  $\chi_2$  ( $\sigma_2$ ) and  $\chi_3$  ( $\sigma_3$ ) 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  $\chi_1$  is an easy axis of magnetization though the sample can be magnetized nearly as easily along  $\chi_3$  as well. Further the large anisotropy and difference in magnetization behavior between  $\sigma_1$  and  $\sigma_2$  is consistent with their corresponding temperature dependencies. The most significant result is that although  $\sigma_1$  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  $\sigma_2$  and  $\sigma_3$ . In fact,  $\sigma_3$  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.<sup>6,7</sup> There are some significant differences in the magnetization data. Our

magnetization data (as well as  $\chi_i$  vs T data) show that the  $\sigma_1$  direction is most easily magnetized. The reason for the discrepancy between our work on a single crystal and the earlier work<sup>6,7</sup> may be understood in terms of the anisotropy of the material. We find that the magnetization in the (ac) plane of MnPc, which contains  $\sigma_1$  and  $\sigma_2$ , 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 ( $\sigma_{\parallel}$ ) and perpendicular ( $\sigma_{\perp}$ ) to the bundle axis (i.e., the b-axis). The  $\sigma_{\parallel}$  from the earlier work<sup>6,7</sup> corresponds to our  $\sigma_3$ , and the  $\sigma_{\perp}$  corresponds to some average of our  $\sigma_1$  and  $\sigma_2$ . Since  $\sigma_1$  and  $\sigma_2$  are very different in magnitude, the experimentally observed average, that is  $\sigma_{\perp}$ , came out to be smaller than  $\sigma_1$ , and consequently, an erroneous conclusion concerning the easy direction was arrived at. The value for  $\sigma_1$  from the earlier work<sup>6,7</sup> is in reasonable agreement with our  $\sigma_3$ ; at 4.2 K we obtained a value of  $12 \times 10^3$  emu for  $\sigma_3$ , while Miyoshi obtained a value of  $14 \times 10^3$  for  $\sigma_1$  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  $\sigma_0$  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  $\sigma_0^{AV}$  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  $90^\circ$ , 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).<sup>5</sup> 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:<sup>6,7</sup>

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

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,<sup>5</sup> 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  $\chi_2$  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  $\chi_1$  and  $\chi_3$  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.<sup>4,6</sup> 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  $90^\circ$  superexchange mechanism, (the Mn-N-Mn angle is nearly  $90^\circ$ ). The  $d$ -electron configuration of the  $Mn^{2+}$  ion in MnPc is  $(b_{2g})^2 (e_g)^2 (a_{1g})^1$ . It has been shown<sup>4</sup> 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.<sup>4</sup>

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,<sup>5</sup> based on the high temperature (80-300 K) single crystal susceptibility data, has shown that the splitting is about  $40 \text{ cm}^{-1}$  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  $\chi_1$ , is rotated  $20^\circ$  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  $\chi_1$  which shows a kink in the  $\chi_1$  versus T curve at  $\sim 3$  K and the temperature independence of  $\chi_1$  below 2 K.
- Figure 7. Single crystal magnetization data at 4.2 K along  $\chi_1$  ( $\sigma_1$ ),  $\chi_2$  ( $\sigma_2$ ), and  $\chi_3$  ( $\sigma_3$ ) 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  $\chi_1$  and  $\chi_3$ .  $T_1$  and  $T_2$  represent the two sites for the tetragonal MnPc molecules.



b-axis



















