Low temperature, high magnetic field investigations of the nature of magnetism in the molecular semiconductor β - Cobalt Phthalocyanine ($C_{32}H_{16}CoN_8$)

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ABSTRACT

Results from detailed investigations of the magnetic properties of a powder sample of β -CoPc for the temperatures $T = 0.4$ K to 300 K and in magnetic fields H up to 90 kOe are reported. X-ray diffraction confirmed the β -phase and scanning electron microscopy showed plate-like morphology of the sample. For $T > 3$ K, the data of magnetic susceptibility χ vs. T fit the Curie-Weiss (CW) law yielding $\theta = -2.5$ K, $\mu = 2.16 \mu_B$ per Co^{2+} and $g = 2.49$ for spin $S = 1/2$ of the low spin-state of Co^{2+} . However for $T < 3$ K, the χ vs. T data deviates from the CW law yielding a peak in χ at $T_{max} = 1.9$ K. It is shown that the χ vs. T data from 0.4 K to 300 K fits well with the predictions of the Bonner-Fisher (BF) model for $S = 1/2$ Heisenberg linear chain antiferromagnet with the Co^{2+} - Co^{2+} exchange $J/k_B = -1.5$ K ($\hat{H} = -2J \sum \mathbf{S}_i \bullet \mathbf{S}_{i+1}$). The data of magnetization M vs. H at $T = 1$ K agrees with the predictions of the BF model with $J/k_B = -1.5$ K, yielding saturation magnetization $M_S = 12.16$ emu/g above 60 kOe corresponding to complete alignment of the spins.

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1. Introduction:

Transition-metal phthalocyanines (TMPc) with the chemical formula $C_{32}H_{16}N_8TM$ are an important class of organic semiconductors with potential applications in gas sensors, photovoltaic cells and field effect transistors [1, 2]. The planar structure of TMPc consists of one TM atom at the center bound to four N atoms (Fig. 1) and because of this special symmetry, the ground state of the TM ions often violates Hunds' rules. Examples are the spin $S = 3/2$ intermediate state for the d^5 Mn^{2+} in β -MnPc [3-5], $S = 0$ state d^8 for Ni^{2+} in NiPc [6] and $S = 1/2$ state for d^7 Co^{2+} in β -CoPc [7, 8]. The TM atoms form a linear chain along the b-axis (Fig.1) and the stack angle δ between the orientation of the molecular plane and the b-axis also affects the magnetic properties, δ being 65° (45°) for the α (β) phase. In general, the exchange coupling between the TM ions in the α -phase is much larger than that in the β -phase as for example reported in CoPc [7,8] and CuPc [9,10] systems.

Fig. 1. Molecular model, unit cell, and molecular arrangement of β -CoPc: $a = 1.4542$ nm, $b = 0.47731$ nm, $c = 1.9352$ nm, $\beta = 120.82^\circ$, and the stack angle $\delta \sim 45^\circ$.

The nature of magnetism in CuPc [9, 10] and β -CoPc [7,8] have been reported to be Heisenberg linear chain antiferromagnetism (HLCA) with spin $S = 1/2$ but without 3-dimensional (3D) long range order following the predictions of the Bonner-Fisher (BF) model. The BF model predicts a broad-peak in the temperature dependence of the magnetic susceptibility χ at a temperature $T_{\max}$ given by $T_{\max} = 1.28 |J|/k_B$ [11] where J is the exchange constant defined by the Heisenberg Hamiltonian: $\hat{H} = -2J\sum \mathbf{S}_i \cdot \mathbf{S}_{i+1}$. For the α -CuPc system, χ vs. T showed a maximum at $T_{\max} = 2.2$ K yielding $|J|/k_B = 1.7$ K [10]. For β -CuPc, the predicted $T_{\max} = 0.25$ K corresponding to $|J|/k_B = 0.2$ K was not accessible in the reported studies [10]. In the recent reported magnetic studies on β -CoPc [7], it was concluded that β -CoPc is also an HLCA with spin $S = 1/2$ and $|J|/k_B = 1.9$ K was determined from the fit of the magnetization M vs. magnetic field (H) data at 2 K to the predictions of the BF model. However, since the reported χ vs. T data were limited to temperatures $T > 8$ K, the observation of $T_{\max}$ characteristic of an HLCA was not observed in β -CoPc [7].

In this paper, we report results of our detailed investigations of the nature of magnetism in β -CoPc covering the wider temperature range of 0.4 K to 300 K and in magnetic fields up to 90 kOe. Following the prediction of the BF model, the data of χ vs. T shows a maximum at $T_{\max} = 1.9$ K corresponding to $J/k_B = -1.5$ K and the data of M vs. H at $T = 1$ K covering the wider magnetic field range also fits the BF model with $J/k_B = -1.5$ K. These results, details of which are presented below, have clearly established β -CoPc as an HLCA with spin $S = 1/2$, $g = 2.49$, magnetic moment $\mu/\text{Co}^{2+} = 2.16 \mu_B$ and nearest neighbor exchange coupling $J/k_B = -1.5$ K between the Co^{2+} ions.

2. Methods and structural properties

The powder sample of CoPc used here was purchased from Alfa Aesar (stock # 41496) and used as received. X-ray diffraction (XRD) analysis of the sample was performed at room temperature using PANalytical X'Pert Pro X-ray diffractometer with Cu-K α source ($\lambda = 0.15418$ nm). The XRD pattern of the sample shown in Fig. 2 agrees with the expected pattern of β -CoPc (ICDD #02-061-3631) with space group $P2_1/c$ and two molecules per unit cell in the monoclinic structure with lattice parameters: $a = 1.4542$ nm, $b = 0.4773$ nm, $c = 1.9352$ nm, and $\beta = 120.82^\circ$ [12]. This structure is shown in Fig. 1. Note that all the observed peaks in the XRD pattern match well with the ICDD pattern for β -CoPc. The lower observed intensity of the (100) peak is likely due to the plate-like preferred orientation of the sample as evident in the scanning electron micrograph of the sample shown in Fig. 3. For scanning electron microscopy, a JEOL 7600 FE-SEM system was used. Measurements of the magnetization (M) from 2 K to 300 K and in magnetic fields up to 90 kOe were carried out using the Physical Property Measurements System (PPMS) manufactured by Quantum Design Inc. Additionally M vs. T data were obtained using a home-made susceptometer from 0.4 K to 20 K with DC field $H = 10$ kOe, frequency = 331 Hz, and ac field $H_{ac} = 3.3$ Oe at the National High Magnetic Field Laboratory (NHMFL) DC field facility SCM2. The ac susceptibility data acquired at the NHMFL was normalized to the DC susceptibility data acquired using the PPMS at a single temperature (20 K). This can be justified because (i) we didn't observe any frequency dependence from the ac susceptibility; and (ii) the temperature dependence is practically identical between the data obtained by the two techniques. In general, if the magnetic relaxation is much faster than the measurement time scale (1 – 10 ms in our case), the ac susceptibility resembles the DC susceptibility, which seems to be the case for β -CoPc at least in the measured temperature range.

Fig. 2. The top panel shows the XRD pattern of β -CoPc sample with Miller indices of major lines marked; the bottom panel shows the ICDD data of β -CoPc.

Fig. 3. Scanning electron micrograph for β -CoPc powder sample. The length of scale bar is 20 μm .

3. Results, analysis and discussion

The temperature dependence of magnetic susceptibility χ measured with applied $H = 10$ kOe is shown in Fig. 4. Since M vs. H is quite linear in H up to about 20 kOe (see inset of Fig. 4 for data at 2 K), $\chi = M/H$ represents the differential susceptibility. Again, the data acquired at the

NHMFL from 0.4 K to 20 K is merged with the data acquired with the PPMS from 2 K to 300 K by normalizing the former with the latter at 20 K. The combined data shows a distinct peak at $T_{\max} = 1.9$ K, which is independent of frequency.

Fig. 4. Magnetic susceptibility χ vs. temperature T of β -CoPc with $H = 10$ kOe. Solid line **A** is fit to the modified Curie-Weiss law: $\chi = \chi_0 + [C/(T - \theta)]$ with the parameters: $\chi_0 = -1.8 \times 10^{-6}$ emu/gOe, $C = 1.02 \times 10^{-3}$ emu-K/gOe, and $\theta = -2.5$ K. Solid line **B** is fit to Bonner-Fisher model (Eq.1) using the above C and χ_0 and $J/k_B = -1.5$ K. The inset shows the M vs. H plot at 2 K.

The analysis of the data was done as follows. First the data acquired from the PPMS from 2 K to 300 K was fitted to the modified Curie-Weiss (CW) law: $\chi = \chi_0 + [C/(T - \theta)]$. For this purpose, $\chi_0 = -1.8 \times 10^{-6}$ emu/gOe was determined by plotting χ vs. $1/T$ and linearly extrapolating the high temperature data to $1/T \rightarrow 0$. This χ_0 includes the diamagnetic contributions of the plastic sample holder and the sample itself. Note that the effect of χ_0 is only noticeable for $T > 100$ K. Next, by plotting $(\chi - \chi_0)^{-1}$ vs. T (see Fig. 5), the linear fit yielded $C = 1.02 \times 10^{-3}$ emu-K/gOe and $\theta = -2.5$ K, the negative θ signifying antiferromagnetic exchange coupling. In Fig. 4,

the solid line marked **A** represents fit to the modified CW law with the magnitudes of χ_o , C , and θ listed above. From Fig. 4, it is quite evident that the data deviates from the CW fit below about 3 K. However, the fit for $T > 3$ K is used to determine the magnetic moment μ using the relation $C = N\mu^2/3k_B$ where N is the number of magnetic ions per gm, each with magnetic moment μ and k_B is the Boltzmann constant. This analysis yields $\mu = 2.16\mu_B$ per Co^{2+} ion and using $\mu^2 = g^2S(S+1)$ yields $g = 2.49$ for the $S = 1/2$ low-spin state of Co^{2+} in $\beta\text{-CoPc}$.

Fig. 5. Plots of the temperature dependence of magnetic susceptibility χ and the inverse magnetic susceptibility $(\chi - \chi_o)^{-1}$ of $\beta\text{-CoPc}$ in $H = 10$ kOe; the solid line for the latter is the linear fit representing the CW law.

The data of χ vs. T for the whole temperature range of 0.4 K to 300 K was next fitted to the prediction of the BF model. The expression given by Feyerherm et al [13] and Eggert et al [14], modified to the Hamiltonian $\hat{H} = -2J\sum \mathbf{S}_i \cdot \mathbf{S}_{i+1}$, is given by $\chi = \chi_o + (C/T)F(x)$ where

$$F(x) = (1 - a_1x + a_2x^2) / (1 - b_1x + b_2x^2 - b_3x^3) \text{ ----- (1).}$$

In Eq. (1), $a_1 = 0.17032$, $a_2 = 0.93404$, $b_1 = 1.46764$, $b_2 = 0.54784$, $b_3 = 4.28544$, and $x = J/(k_B T)$. Since J is negative for antiferromagnetic interaction, all terms in Eq. (1) are positive. The line **B** in Fig. 4 is the best fit to Eq. (1) using $J/k_B = -1.5$ K and $C = 1.02 \times 10^{-3}$ emu-K/gOe, the latter determined earlier from the CW fit for $T > 3$ K. In addition, using the observed $T_{\max} = 1.9$ K $= 1.28|J|/k_B$ according to the BF model also yields $|J|/k_B = 1.5$ K. Thus the observation of $T_{\max}$ and the overall fit of the data to Eq. (1) of the BF model with $J/k_B = -1.5$ K provides convincing evidence for the accuracy of this analysis. This magnitude of J/k_B is somewhat smaller than $J/k_B = -1.9$ K reported by Serri et al [7] which was determined from the fit of the M vs. H data at 2 K. Our analysis of the M vs. H taken at $T = 1$ K is given next.

The data of M vs. H at 1 K and 5 K bracketing $T_{\max} = 1.9$ K are shown in Fig. 6. The data at 1 K was acquired at the NHMFL, whereas the data at 5 K were taken at West Virginia University using the PPMS. The expected value of the saturation magnetization $M_S = Ng\mu_B S$ is calculated to be 12.16 emu/g using $g = 2.49$ and $S = 1/2$ which agrees well with the measured value in Fig. 6 at $T = 1$ K where the data is saturated. The Bonner-Fisher paper on the HLCA [11] does not provide an analytical expression for M vs. H but provides calculated plots of M vs. H for several $k_B T/|J|$ valid for $N = 10$ spins in the chain. **Therefore we used the internet-available software “digitizer” to reproduce the M vs. H plots of [11]. This software allows one to take a scanned image of a plot and digitize values off the plot by clicking the mouse on each data point. The data can then be saved and plotted. By following this procedure, we have digitized those plots from the original paper [11] and re-plotted them. Using $|J|/k_B = 1.5$ K evaluated in this work from the fit of χ vs. T data, the red line (marked as $T = 0.9$ K, $|J|/k_B = 1.5$) in Fig. 6 represents fit to the BF model for the available curve of $k_B T/|J| = 0.6$ [11]. Overall, the agreement with the experimental data taken at 1 K is quite satisfactory considering that the BF curves are calculated**

for $N = 10$ spins in a chain rather than for an infinite chain. The agreement is excellent for $H < 30$ kOe, the region where the BF curves appear to be less sensitive to the magnitude of J . This is the region used by Serri et al [7] to fit their data at 2 K to evaluate $|J|/k_B = 1.9$ K. Because of this, it is suggested that the smaller magnitude of $|J|/k_B = 1.5$ K evaluated here from $T_{\max}$ and the fit to the χ vs. T from 0.4 K to 300 K is likely more accurate. Also, using $|J|/k_B = 1.9$ K by Serri et al [7], the green line (marked as $T = 0.95$ K, $|J|/k_B = 1.9$) in Fig. 6 represents fit to the BF model for the available curve of $k_B T/|J| = 0.5$ [11]. Clearly, the curve corresponding to $|J|/k_B = 1.5$ K fits better than the curve corresponding to $|J|/k_B = 1.9$ K which further confirms that $|J|/k_B = 1.5$ K from this work is more accurate than $|J|/k_B = 1.9$ K.

For the M vs. H data at 5 K, fitting the data to the BF model was not possible since the closest calculated available curve to 5 K from Ref. 11 is for $k_B T/|J| = 3.0$ which corresponds to $T = 4.5$ K. Since the fit of the χ vs. T data to the Curie-Weiss law is valid for $T > 3$ K (Fig. 5), we have fitted the M vs. H data at 5 K to the prediction of the molecular-field model which for spin $S = 1/2$ yields the variation [15]

$$M = M_S \tanh\{g\mu_B H/[2k_B(T-\theta)]\} \text{ ----- (2)}$$

In the above, the CW variation is taken into account by including θ . The fit of the data at 5 K to Eq. (2) using the experimental $\theta = -2.5$ K, $g = 2.49$ and $M_S = 12.16$ emu/g, shown as solid line in Fig. 6, is quite good.

Fig. 6. Magnetization M vs. H data for β -CoPc at 1 K (black solid line) and 5 K (open circles) are compared respectively with the predictions of the Bonner-Fisher model at 0.9 K with $|J|/k_B = 1.5$ K (red line) and 0.95 K with $|J|/k_B = 1.9$ K (green line). The blue line fitting the data at for 5 K represents Eq. (2).

4. Conclusions:

The results of χ vs. T and M vs. H data covering the temperature range of 0.4 K to 300 K and in H up to 90 kOe convincingly show Heisenberg linear chain antiferromagnetism in β -CoPc with $J/k_B = -1.5$ K. The observation of $T_{\max} = 1.9$ K and fits of the χ vs. T data and the isothermal M vs. H data at 1 K to the Bonner-Fisher model are the important new results. The range of validity of the Curie-Weiss law in β -CoPc for $T > 3$ K is also established.

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Graphical Abstract