Magnetic properties of linear metal chains and their liquid crystal derivatives

David P. Elam
Department of Physics, University of Florida
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Abstract

This work examined the magnetic properties of the linear metal chains Fe(bipy)Cl$_2$ and Fe(bipy)Br$_2$ and their liquid crystal (LC) derivatives. All the materials experienced long range order in the temperature range of 6-8 K. Fe(bipy)Cl$_2$ showed behavior which may be due to antiferromagnetic ordering. Measurements of Fe(bipy)Br$_2$ and its LC derivatives point toward a possible spin cross over between 50 and 300 K. The measurements were performed with a Quantum Design MPMS SQUID magnetometer in the temperature range of 2-300 K and in a field between 0-7 T.

I. Introduction

A. Liquid Crystals

The main difference between solids and liquids is in how their atoms or molecules are arranged with respect to one another. The molecules in a crystalline solid are arranged in a distinct pattern that repeats itself throughout the entire crystal. This pattern is called long range ordering. The ordering in a solid is both orientational and translational. In other words, the molecules in a solid are fixed in a specific orientation and position in space. Liquids, however, do not share the long range ordering found in solids. The molecules in a liquid are arranged in a more or less random fashion over the entire liquid.

Some materials exhibit an intermediate phase between the solid and liquid phases. This phase is commonly known as the liquid crystalline phase. This phase possesses both the long-range order of solids and the short-range order of liquids. For example, as a liquid crystal is cooled down from the liquid phase, it first forms the nematic phase. In the nematic phase all the molecules in the material align themselves in one direction, thus assuming orientational order. Even though the molecules are all aligned in the same
direction, they are still randomly positioned in the liquid. As the liquid is cooled further, it undergoes another phase transition into either the smectic A or C phase. In both of these phases the molecules maintain the orientational order of the nematic phase, but they gain some degree of translational order. The molecules gain translational order in that they form layers. In each layer the molecules are ordered in space, but there is no correlation in the positions of the molecules from one layer to the next. The difference between the smectic A and C phases is in the A phase the molecules are pointing perpendicular to the plane of the layer. In the C phase the molecules are pointing in some direction away from the perpendicular [1].

B. Linear Metal Chains

Linear metal chains are coordinate compounds of metal ions that are linked together to form long polymer chains. The metal ions are typically linked together or bridged by anions like Cl\(^-\) or Br\(^-\) as shown in Fig. 1. This bridge between the metal ions can serve as a pathway for magnetic exchange interactions between the metals [2].

![FIG. 1: The metal-metal bridging mechanism for linear metal chains.](image-url)
C. Purpose

The ability to develop practical applications of one-dimensional magnets depends in part on the ease in which crystals of these materials can be grown. One possible solution to this problem is the incorporation of liquid crystal properties in these low dimensional magnets. In addition, annealing and then recooling the liquid crystal could repair defects in its crystal structure. The ability to easily repair defects in the structure of liquid crystals is a large advantage over solid crystals. This application has made metal containing liquid crystals an attractive area of study [3]. The purpose of this experiment was to investigate the magnetic properties of the iron containing linear chains Fe(bipyridine)Cl₂, Fe(bipyridine)Br₂, and their liquid crystal derivatives.

II. Experiment

A. Equipment

The magnetic measurements were made using a Quantum Design MPMS SQUID (Superconducting QUantum Interference Device) magnetometer. The MPMS consists of three major components: the 7 T superconducting magnet, the SQUID detection system, and the sample probe. The SQUID itself (the details of its operation will not be discussed here) does not directly make the magnetic measurements. It instead employs a second derivative detection coil to pick up the signal from the sample. The function of the detection coil is to screen out the overwhelming uniform magnetic field from the superconducting magnet and any external fields so that the small signal from the sample can be accurately measured. This coil makes the system insensitive to any drifts in the magnetic field from the superconducting magnet. This feat is accomplished by using two
counter but equally wound coils. Since external magnetic field lines will transverse both coils, equal and opposite currents will be produced. The external field will therefore induce zero net current in the coil. However, the magnetic field produced by the sample will be picked up by one coil at a time due to the relatively small size of the sample as compared to the size of the coil. Thus, the detection coils monitor the magnetic moment from the sample while canceling out other external signals.

B. Materials

The materials studied in this experiment were Fe(bipyridine)Cl₂ and Fe(bipyridine)Br₂ along with their liquid crystal derivatives, see Table I.

<table>
<thead>
<tr>
<th>Material</th>
<th>Label</th>
<th>Color</th>
<th>Formula Weight (g/mol)</th>
<th>Sample mass (mg)</th>
<th>gelcap mass (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(bipy)Br₂ (Parent)</td>
<td>LAH2-38</td>
<td>dark red</td>
<td>371.97</td>
<td>68.59</td>
<td>43.25</td>
</tr>
<tr>
<td>Fe(4,4'-C14-bipy)Br₂</td>
<td>LAH2-43</td>
<td>dark red</td>
<td>1824.04</td>
<td>22.15</td>
<td>42.90</td>
</tr>
<tr>
<td>Fe(5,5'-C14-bipy)Br₂</td>
<td>LAH2-44</td>
<td>dull orange</td>
<td>1824.04</td>
<td>41.52</td>
<td>42.62</td>
</tr>
<tr>
<td>Fe(bipy)Cl₂ (parent)</td>
<td>LAH2-18</td>
<td>brick red</td>
<td>283.06</td>
<td>88.08</td>
<td>42.40</td>
</tr>
<tr>
<td>Fe(4,4'-C14-bipy)Cl₂</td>
<td>EAM1-28</td>
<td>dark red</td>
<td>1735.13</td>
<td>49.16</td>
<td>43.16</td>
</tr>
<tr>
<td>Fe(5,5'-C14-bipy)Cl₂</td>
<td>STS1-18</td>
<td>light red</td>
<td>1735.13</td>
<td>25.20</td>
<td>32.59</td>
</tr>
</tbody>
</table>
The C14 notation from Table I is defined in Fig. 2b as long carbon chains attached to the bipyridine ring. The carbon chains are each 14 atoms long. These molecules form a polymer chain with six coordinate iron(II). The iron(II) ions are bridged by either Cl or Br as shown in Fig. 1. All six of the samples were measured as a sticky powder and were prepared by Williams College.

C. Procedure

In preparation of the magnetic studies, all of the materials were packed and weighed in a gelcap with the exception of STS1-18. We were unable to prepare STS1-18 in a gelcap because there was very little material to work with. Its magnetic moment was also small which made centering of the sample in the SQUID detection coils difficult. For these reasons, STS1-18 was instead packed between two gelcap tops as shown in Fig. 3.
The packed gelcap was then mounted and secured in an ordinary straw. The straw was attached to the end of the sample probe with tape (FIG. 4). For more information on mounting the sample, see the MPMS hardware manual [4].

The magnetic moments of the materials were measured in a field of strength 100 Oe. The samples were first cooled in a zero field from 300-2K. The temperature of
the sample was then slowly increased to 10K with the SQUID making magnetic moment measurements every 0.5K. The temperature interval between measurements was increased as the sample once again approached 300K. At 300K the material was cooled a second time to 2K under an applied field of 100 Oe. Field cooled data were only taken up to 10K. Finally, the temperature of the sample was held constant at 5K, and the moment of the material was measured as the magnetic field was increased from 0-7 T. The gelcap background and the core diamagnetism were subtracted from all the data.

III. Results

The Curie-Weiss law, eq. (1), provides a fairly good fit to the $\chi$ Vs. T data for the chlorine compounds. The results of these fits are presented in Fig. 5 and Table II.

$$\chi = \chi_0 + C/(T-\theta); \quad C = (N\mu_B^2 S(S+1))/3k_B$$

(1)

<table>
<thead>
<tr>
<th>Material</th>
<th>Label</th>
<th>C (emu*K/mol)</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(bipy)Cl$_2$ (parent)</td>
<td>LAH2-18</td>
<td>0.59</td>
<td>-1.6</td>
</tr>
<tr>
<td>Fe(4,4'-C14-bipy)Cl$_2$</td>
<td>EAM1-28</td>
<td>0.66</td>
<td>-0.29</td>
</tr>
<tr>
<td>Fe(5,5'-C14-bipy)Cl$_2$</td>
<td>STS1-18</td>
<td>0.46</td>
<td>-4.4</td>
</tr>
</tbody>
</table>

TABLE II: The Curie constant and $\theta$ for the chlorine materials were produced from the best fits of the data.
Fig. 5: $\chi$ vs $T$ for the chlorine materials. The solid lines are Curie-Weiss fits of the data.

Fig. 6: $\chi T$ vs $T$ plot of the chlorine materials. The increase in $\chi T$ from zero in the low temperature range suggests antiferromagnetic ordering.
Fig. 7: The increase in $\Delta M$ which begins at about 8K indicates long range ordering.

$\Delta M = \text{M}_{\text{field cooled}} - \text{M}_{\text{zero field cooled}}$

Assuming the Curie-Weiss law is a good approximation of the data, the plot of $\chi T$ Vs. $T$ implies that the chlorine containing materials may be ordering antiferromagnetically (FIG. 6). The result of a negative $\theta$ from the fits of all three materials supports this idea. Also, long range ordering appears to set in around 8K. This is supported by the increase of $\Delta M$ in Fig. 7. The result of antiferromagnetism directly contradicts previous reports that Fe(bipy)Cl$_2$ orders as a ferromagnet at 4K [5]. Sorting out this discrepancy may be a good goal for future study of these materials.

The behavior of the bromine materials is very different from that of the chlorine compounds (Fig. 8). The maximum in $\chi$ and the "S" shape of the $\chi T$ Vs. $T$ plots indicate a spin crossover from a high spin state to a low spin state [6-7].
Fig. 8: $\chi$ vs $T$ for the bromine containing materials. The maximum shows possible spin crossover behavior.

Currently, the increase of $\chi$ in a Curie like fashion can only be attributed to impurities in the sample that are behaving as free spins. However, the percentage of
impurities required to produce this effect has not yet been checked for plausibility. The increase in $\Delta M$ (Fig. 9) suggests that the bromine materials order around 6-8K. The type of long range ordering that the bromine compounds exhibit is uncertain, but it is reasonable to assume that the bromine and the chlorine compounds have the same type of ordering [8]. In addition, both materials did not follow the Brillouin function at 5 K (FIG. 10). Since the Brillouin function describes non-interacting spins, the fact that these materials do not follow the Brillouin at 5 K is further evidence of ordering below 10 k.

Fig. 9: The increase in $\Delta M$ which begins at about 8K indicates long range ordering. $\Delta M = M_{\text{field cooled}} - M_{\text{zero field cooled}}$
Fig. 10: The plot to the right shows the M vs B data for the Cl materials. The plot on the left shows the data for the Br materials. The solid lines represent the best fits of the data to the Brillouin function.

IV. Acknowledgements

I would like to thank the National Science Foundation and the National High Magnetic Field Laboratory for funding my research this summer. I would especially like to thank Dr. Mark W. Meisel for allowing me to collaborate with him over the summer. I would also like to thank Dr. Lee Y. Park for providing us with the materials used in the experiment and for providing us with detailed information about these materials. I would also like to thank Dr. Dan Talham for his help with the chemical structures of the materials. I would like to thank Erik Cizmar and Ju-Hyun Park for all the help they gave me with the SQUID magnetometer. I would also like to thank James Davis and Angela Stewart for their collaboration with me on this project.
V. References


[6] Mark W. Meisel (private communication)
