SURFACE MAGNETISM IN ORGANIC CHARGE TRANSFER SALTS

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It is generally thought that lattice defects can give rise to important effects in the electrical and magnetic properties of organic charge transfer salts. In an attempt to clarify the role of defects we have investigated the effect of strong pressing on the static magnetic properties of several charge transfer salts with TCNQ (tetracyanoquinodimethane) as the acceptor molecule. Pressing is expected to introduce lattice defects, to decrease the average chain length and also to increase the surface area of the materials. The salts were initially small single crystals, they were pressed in a Cu-Be die taking care to avoid magnetic contamination and after pressing they were fine powders, particle size 1μ or less.

Up to now we have studied several compounds, including TTF-TCNQ which has a high electrical conductivity and shows a metal-insulator transition at low temperatures, $Qn(TCNQ)_2$ also a good conductor but in which inherent disorder is important and Cs_2 $(TCNQ)_3$ which is a semiconductor at room temperature.

Magnetisation-field (M-H) curves were measured at several temperatures both before and after different degrees of pressing. Before pressing all materials show linear M-H plots, examples of which are shown in figure 1 marked with 0. For Qn $(TCNQ)_2$ and TTF-TCNQ the values of the room temperature susceptibility are in agreement with those in the literature[(1,2)].

However a new result of the present work is that for $Qn(TCNQ)_2$ pressing gives rise to substantial curvature in M-H at room temperature as shown in figure 1,i.e. to a large saturating magnetisation which increases steadily with increased pressing. The saturation magnetisation is approximately 2.5, 15 and 39 emu/mole for pressing levels of 5, 15 and 40 x 10^3 kg wt/cm^2 respectively. With S = 1/2 this corresponds to 0.07, 0.4 and 1% of donor molecules.

As shown in the inset to figure 2 the saturating component is only weakly temperature dependent, indicating a strong coupling of spins even at room temperature.

In figure 2 we also show $\chi(T)$ for Qn $(TCNQ)_2$ before and after pressing in the latter case χ was determined from the high field slope of the M-H curve. Bearing in mind the large core diamagnetism (-4.2 10^{-4} emu/mole) which is not changed by pressing we conclude that the spin susceptibility is only altered by 30% or so.

Similar effects are observed for the semiconducting salt Cs_2 $(TCNQ)_3$ but interestingly not for TTF-TCNQ as shown in figure 1.

Recently we have made further experiments on $Qn(TCNQ)_2$ and TTF-TCNQ. We have also povdered the two materials using a vibrating mill and obtained results consistent with those obtained by pressing. It has been suggested that finely powdered $Qn(TCNQ)_2$ is strongly affected by exposure to air, so we have also made some experiments in which samples were powdered in a helium gas atmosphere and then measured without exposure to air. Again consistent results were obtained and subsequent exposure to air caused no further changes in the room temperature M-H curve of Qn $(TCNQ)_2$.

Since the effect occurs for both conducting Qn $(TCNQ)_2$ and semiconducting Cs_2 $(TCNQ)_3$, i.e. is independent of the electronic structure near the Fermi level, this seems to imply that the spins are not coupled through the bulk of the material.

We believe that the effect is due to the enhanced surface area of the pressed materials and claim that surface magnetism is observed in these organic charge transfer salts. It has been proposed by M.H.Cohen [(3)] that charge transfer could be absent near the surface of these materials. For some donor molecules the absence of charge transfer leads to one unpaired spin per donor site, i.e. the neutral donor has an unpaired electron spin. This is the case for Qn and Cs. Whereas for others such as TTF the neutral donor molecule has no unpaired spin. The presence of a large saturating magnetisation for the pressed Qn and Cs salts on the one hand and the absence for pressed TTF-TCNQ on the other hand seems to strongly support the above picture.

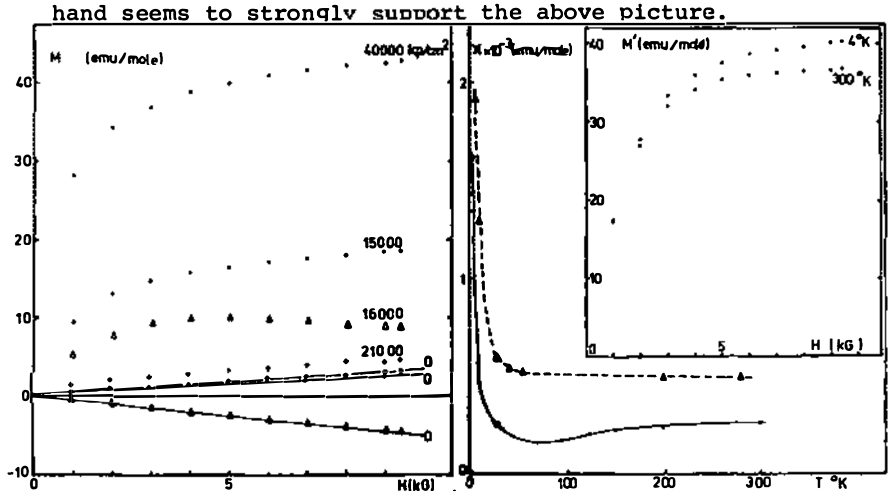

Figure 1. M-H measurements at 295 K for Qn $(TCNQ)_2$ /•/, $Cs_2(TCNQ)_3$ /Δ/ and TTF-TCNQ /+/. The degree of pressing is indicated by numbers in kg wt/cm^2 (kp/cm^2).

Figure 2. Temperature dependence of susceptibility for $Qn(TCNQ)_2$ unpressed /•/ and pressed /▲/. Inset shows M´-H ($M' = M_{press.} - M_{unpress}$) for Qn $(TCNQ)_2$ at two temperature.

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