Magnetic properties of DCNQI salts studied using μSR

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Abstract

Examples from the \((R_1R_2\text{-DCNQI})_2X\) family of molecular conductors have been studied using μSR in order to provide information about the microscopic magnetic properties of the various phases. For the fully deuterated dimethyl Cu salt \((d_2\text{-DMe-Cu})\) there is a metal-insulator (MI) transition around 80 K and a magnetic transition around 7 K. The muon spin relaxation rate becomes enhanced in the region of the MI transition and below, reflecting the quenching of valence fluctuations and the appearance of localised spins on the Cu sites. A zero field precession signal develops below 7 K as a result of the 3D magnetic ordering of the Cu spins; the field distribution derived from the precession frequency is consistent with the proposed magnetic structure. In addition to the zero field studies, nuclear quadrupolar level crossing resonance between the muon and the imine nitrogen of the DCNQI has been used to study the temperature dependence of the electronic state of the molecular conductor.

Keywords: Organic conductors based on radical anion salts, Magnetic measurements, Metal-insulator phase transitions, Magnetic phase transitions.

1. Introduction

The copper salt of the organic molecule DMe-DCNQI is a metal with a structure consisting of columns of Cu atoms separated by stacks of molecular spacers. Interaction between the Cu columns takes place through the DCNQI molecules [1,2] with no direct inter-column overlap of the Cu atoms. The electrical and magnetic properties are thus highly sensitive to pressure and to 'chemical pressure' produced by modifications of the molecule such as selective deuteration. A rich phase diagram has been established for this system, involving charge and spin ordering and associated metal-insulator (MI) transitions with a re-entrance of the metallic state at low temperature [1,2]. In order to provide further information about the microscopic magnetic properties of the various phases we have carried out a series of μSR studies.

Samples were prepared as described elsewhere [2] and took the form of polycrystalline arrays of small needle crystals. The majority of the measurements were made at the ISIS muon facility. For the zero field studies the background magnetic field was compensated to better than 30mG. Full diamagnetic asymmetry was observed in all samples at all temperatures, indicating that no stable paramagnetic muonium states are formed.

2. Spin localisation

Zero field relaxation is sensitive to both nuclear and electronic spins. The metallic salts for both Li and Cu show a general decrease in dipolar width with increasing temperature which is believed to be dominated by the nuclear contribution (Fig.1a) although the Li salt also shows an unexplained peak around 200K.

![Fig.1](image-url) Temperature dependence of the second moment derived from muon spin relaxation in zero field; (a) systems which are metallic at all temperatures and (b) systems showing the MI transition.

Deuteration has the effect of reducing the nuclear contribution to the second moment and introducing the MI transition. Above the MI transition the average spin per Cu is \(\mu_B/3\) whereas below the transition a 3-fold superlattice structure develops with the full \(\mu_B\) on just one in three of the Cu. The Cu contribution to the second moment at the muon may thus increase by up to a factor of 3 below the transition. The second moment for the deuterated...
MI systems is shown in Fig. 1b. The d_2 sample shows the reduced moment expected for 25% deuteration; the high temperature step follows the h_4 sample but an additional increase in the moment comes in below 50 K, reflecting the increasing contribution from localised Cu spins below the 55K MI transition. In the fully deuterated d_4 sample, the Cu spins provide a significant contribution to the moment at low temperature and a clear transition is seen with midpoint around 120 K. This is considerably higher than the MI transition measured at 80 K from conductivity and spin susceptibility and suggests that freeze out of the Cu valence fluctuations on the muon timescale occurs well before the insulating state develops.

3. Magnetic transition

The evolution of the muon spin relaxation signal with temperature in the fully deuterated d_8 sample is shown in Fig. 2a.

A zero field precession signal rapidly develops below 7 K and this reflects the onset of 3D magnetic ordering of the Cu spins. Fig. 2b shows the maximum entropy reconstruction of the local field spectrum where a highly asymmetric field distribution is observed, which is dominated by a pair of lines near 30 G and extends up to the region of 80 G. A model for the antiferromagnetic structure has been proposed [3] where the Cu^{2+} spins are coupled by superexchange through DCNQI dimers. The magnetic structure leads to six inequivalent sites for one general site in the non-magnetic phase. Calculations of the local field distribution for this model [4] show that the local field is close to 30 G for the inner ring of the DCNQI linking Cu to Cu^{+} whereas the DCNQIs linking Cu^{+} to Cu^{2+} have much larger local fields and could be responsible for the higher field components seen in Fig. 2b. No site associated with the Cu stacks has low enough field to be consistent with the measurements.

4. Quadrupolar level crossing resonance

In all samples at low temperatures it is found that the muon spin relaxation rate in longitudinal field shows a marked resonance in the region of 50 G where the second moment reaches approximately one third of its zero field value (e.g. see Fig. 3a). This is the result of a level crossing between the muon Zeeman splitting and the level splitting of a quadrupolar nucleus in an electric field gradient which may be chemically or muon induced.

The resonance amplitude in the d_4-DMe-Cu sample is observed to increase in the vicinity of 100 K but disappears by 150 K (Fig. 3b). This resonance can be compared with the QLCR first seen in Cu metal at 80 G [5]; the resonance width here (FWHM = 6.0 ± 0.9 G) is much narrower than that seen previously in Cu (FWHM = 22 G) and its position would imply close proximity of the muon to Cu (-2Å), which would be inconsistent with the characteristic local field seen in the magnetic state. In contrast, nitrogen QLCR resonances are relatively narrow [6] and this resonance has been assigned to interaction with an imine nitrogen[4]; this is consistent with the muon site associated with the inner ring of the DCNQI, implied by the local field distribution in the ordered state. The QLCR has also been measured in metallic DMe-Li and DI-Cu salts (Fig. 4). Observation of the resonance in DMe-Li is again consistent with the N assignment. In the Li case the resonance is relatively strong and narrow whereas the DI-Cu resonance is comparatively broad and weak; this may be a result of the enhanced electron correlations reported for the DI-Cu salt [7].

References