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μSR studies of magnetic superconductors based on the BETS molecule

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Abstract

Muon spin rotation and relaxation measurements have been made on the molecular magnetic superconductors κ-BETS$_2$FeCl$_4$ and κ-BETS$_2$FeBr$_4$ and the non-magnetic molecular metals κ-BETS$_2$GaCl$_4$ and λ-BETS$_2$GaCl$_4$. In the magnetic materials, zero field muon spin relaxation signals show the formation of static antiferromagnetically ordered states and multiple precession frequencies are observed, corresponding to muon sites situated both within the anion layers and within the BETS layers. Studies of the relaxation behavior in the FeCl$_4$ salt have previously shown significant changes around its superconducting transition and the FeBr$_4$ salt reveals similar changes in the region of its superconducting transition, whose onset is around 1.5 K. In the non-magnetic GaCl$_4$ salts the formation of a superconducting vortex lattice was observed and the penetration depth λ was derived from the transverse field muon relaxation. When the BETS superconductors are compared with the ET-based superconductors that we have already studied using μSR, a striking correlation was observed between T_c and λ^{-3}.

Keywords: BETS; Superconducting transition; Muon

1. Introduction

A relatively recent development in the field of molecular magnetism has been the discovery of molecular systems combining magnetic order of local moments with a metallic conductivity which is retained at low temperatures, leading eventually to superconductivity.

The first example of an organic superconductor containing magnetic anions was a BEDT-TTF salt discovered by Kurmoo et al. [1]. Subsequently much work has been focused on salts based on the BETS molecular donor [2], where many have been found to be metallic and superconducting [3]. In particular, several salts of the form BETS$_2$X, where X is a magnetic anion such as FeBr$_4$ or FeCl$_4$, are found to maintain good metallic and superconducting properties in the presence of magnetic order [4]. In the κ phase materials, which are the main focus of the work presented here, the crystal structure is an orthorhombic layered form in which the BETS molecules are arranged in 2D sheets of interacting dimers in the *ac* plane. These sheets alternate with layers of magnetic anions as one goes along the *b* axis. The spatial separation of the highly conducting molecular layers and the strongly magnetic layers is a key feature of this structure. Magnetic and transport measurements on the FeBr$_4$ salt indicate that the Fe^{3+} is in a high spin state ($S = 5/2$) with an antiferromagnetic transition at $T_N \sim 2.5$ K and a superconducting transition taking place at $T_c \sim 1$ K [5,6]. The *ac* susceptibility measurements of Otsuka et al. [7] indicated that the transition temperatures for the FeCl$_4$ salt were significantly lower than for the FeBr$_4$ salt, with transitions estimated at $T_N \sim 0.65$ and $T_c \sim 0.1$ K. Observations of

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both anisotropic torque and a spin flop transition [8,9] were found to be consistent with antiferromagnetic ordering with the easy axis along *b*, i.e. perpendicular to the highly conducting layers, whereas easy axis along a was deduced for the $FeBr_4$ salt [10]. The non-magnetic λ-$BETS_2GaCl_4$ salt is known to superconduct at ~6 K at ambient pressure [11], whereas κ-$BETS_2GaCl_4$ was previously known to remain metallic down to 0.45 K [12].

These examples of metallic molecular magnets are interesting as they show a Kondo coupling between the localised d-electron moments at the Fe and the delocalised band electrons originating from the molecular pi orbitals. This leads to spin polarisation of the band electrons and results in an indirect RKKY type contribution to the coupling between the localised magnetic moments. An extensive theoretical study of the effect of localised spins on the quasi-2D electronic properties of organic metals such as the BETS salts was recently reported [13], in which the interaction between localised and delocalised states in the κ phase was considered self consistently within a mean-field approximation and was predicted to lead to a commensurate spin density wave (SDW) state in the molecular layers coupled with the magnetic ordering of the Fe in the anion layers.

The magnetic coupling is stronger than the superconducting interaction in these systems, so the superconducting transition takes place within the magnetically ordered phase. From the point of view of the magnetic interactions, the onset of superconductivity will have the effect of removing the RKKY coupling mechanism and any SDW polarisation associated with it. Thus careful studies of the magnetic properties on going through the superconducting transition can be used to give information about the relative contributions of RKKY exchange via the BETS molecular layers and superexchange via Cl or Br atoms within the anion layer.

In a previous paper we presented the first muon spin relaxation measurements on the κ-$BETS_2FeCl_4$ salt [14]. In this paper we report further muon studies of the magnetic and superconducting states of κ-$BETS_2FeBr_4$ and the superconducting states in non-magnetic κ- and λ-phases of $BETS_2GaCl_4$.

2. Experimental

Crystals of κ-$BETS_2FeCl_4$, κ-$BETS_2FeBr_4$ κ-$BETS_2GaCl_4$ and λ-$BETS_2GaCl_4$ were prepared using the methods previously reported in the literature [2,4]. The κ phase forms plate like crystals with the surface of the plate being the *ac* plane and the λ phase forms needles elongated along c. The samples consisted of mosaics of ~40–70 mg of crystals. Measurements with high time resolution were taken at the LTF and GPS instruments at the Paul Scherrer Institute (PSI). Most of the measurements were made under zero field (ZF) conditions where any muon precession signals observed reflect internal fields in the sample produced by its own magnetism. Some measurements were also made with longitudinal field or transverse field (TF) applied to the sample. To measure slower muon spin relaxation component signals over a wider time range additional measurements were also carried out using the μSR instrument at ISIS. The initial muon spin polarisation in each case was perpendicular to the plane of the mosaic, i.e. along the *b* axis.

3. Results and discussion

3.1. Magnetic transitions

The temperature dependence of the time-averaged forward–backward positron asymmetry measured for ZF over the magnetic transition regions for κ-$BETS_2FeCl_4$ and κ-$BETS_2FeBr_4$ are shown in Fig. 1. The magnetic transitions are clearly seen from the reduction of asymmetry on cooling through the transition. The Neel temperatures estimated from the midpoints of the transitions are 0.45 and 2.7 K. The amplitude of the transition in the $FeBr_4$ case is smaller than for $FeCl_4$, which might reflect the difference in the easy axis direction between the systems. However the relatively small mass of the samples made it difficult to prevent a significant fraction of the muons from stopping in the silver sample holder and silver foil degraders, making a

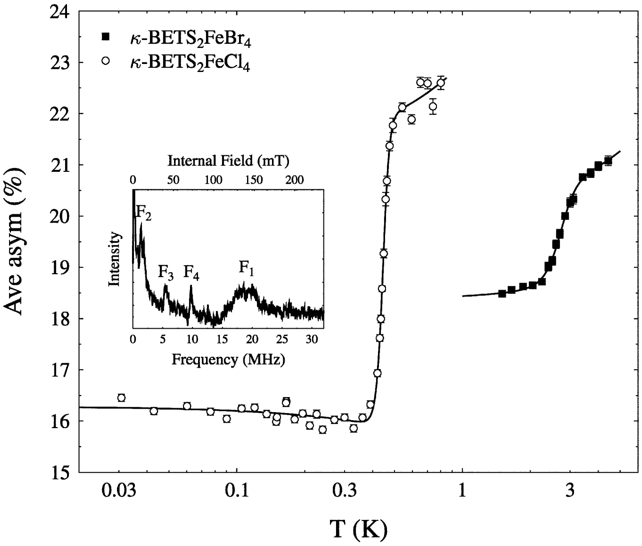

Fig. 1. The antiferromagnetic transitions in two BETS salts measured by ZF μSR. The midpoints of the transitions are at 0.45 K ($FeCl_4$ salt) and 2.7 K ($FeBr_4$ salt). The inset shows the precession frequency spectrum of the ordered state in the $FeCl_4$ salt.

reliable quantitative comparison of the transition amplitudes rather difficult.

The time resolved signal for the $FeCl_4$ salt below the transition shows a complex multicomponent precession. The frequency spectrum of this signal is shown in the inset to Fig. 1, which is derived from co-added data from a number of runs in the 30–200 mK range where the magnetic order is well established and only weakly temperature dependent. The complex precession spectrum in the ordered state of κ-$BETS_2FeCl_4$ contains frequencies ranging from 1 to 20 MHz [14]. We have now measured the precession signal for the κ-$BETS_2FeBr_4$ salt in its ordered state, which also contains a number of frequency bands, which need particularly high statistics data to resolve because of the small precession amplitude compared to the $FeCl_4$ salt (Fig. 2).

3.2. Changes in the magnetic properties on entering the superconducting state

Although we do not so far have sufficiently high statistics data to resolve the detailed temperature dependent behavior of individual precession components in κ-$BETS_2FeBr_4$ in the way that we did for κ-$BETS_2FeCl_4$ [14], we can nevertheless study the time-averaged asymmetry in the magnetically ordered state to search for signs of any influence of the formation of the superconducting state on the magnetic coupling strength between the Fe atoms. Fig. 3 shows the time-averaged asymmetry in the region of the superconducting transition and below. The asymmetry is seen to show a clear dip on cooling through T_c, suggesting an increase in muon spin relaxation or a change in precession frequency at one or more of the muon probe sites. It is also noticeable that the lost polarisation recovers partially on cooling to temperatures well below T_c.

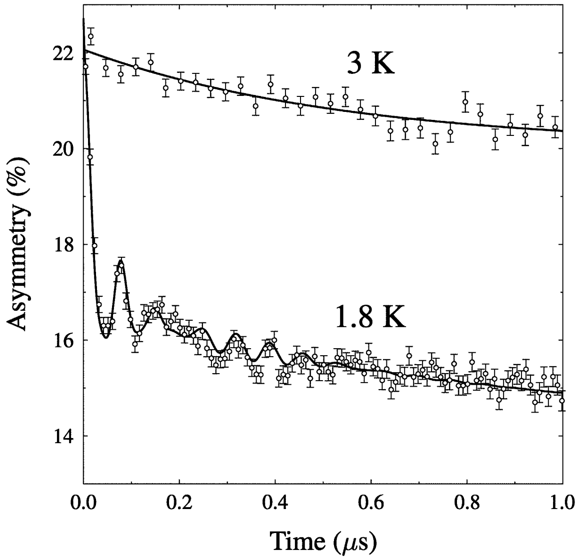

Fig. 2. Muon spin relaxation above and below the antiferromagnetic transition in κ-$BETS_2FeBr_4$. A high statistics run (232 Mevents) at 1.8 K shows a complex precession pattern, which can be represented by the sum of three major precession bands at ~13, ~16 and ~27 MHz (solid line).

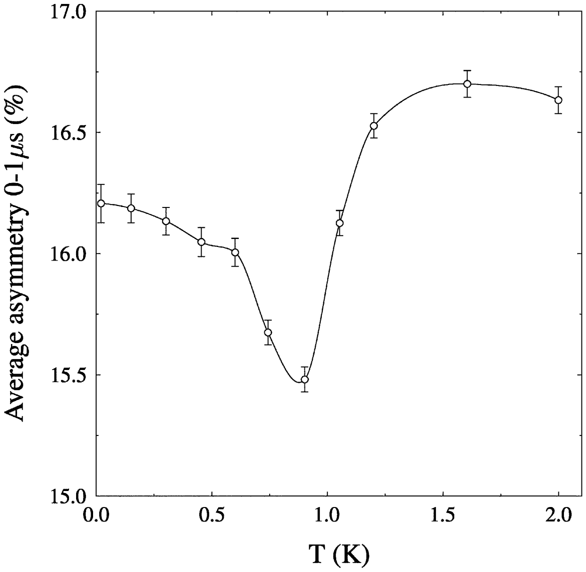

Fig. 3. Temperature dependence of the average asymmetry in the region of T_c and below for κ-$BETS_2FeBr_4$. The line is a guide to the eye.

3.3. Superconducting properties of non-magnetic BETS phases

The presence of magnetism within the whole of the superconducting phases makes quantitative study of the superconducting properties of the magnetic salts rather difficult. However there exist isostructural gallium halide versions of the iron halide magnetic salts, whose superconducting transition temperatures are known or expected to be very similar. We have made TF muon spin relaxation measurements on two of these non-magnetic salts in order to study their superconducting vortex properties. Fig. 4 compares the temperature dependent linewidth obtained in two types of $GaCl_4$ salt. The high transition temperature λ phase salt ($T_c = 5.5$ K) has a large increase in linewidth in the superconducting phase, whereas the κ phase salt has a considerably smaller transition temperature at ~150 mK and the corresponding change in TF linewidth is extremely small.

3.4. Correlation between T_c and λ in BETS and ET superconductors

The magnetic penetration depth λ in the superconducting state can be derived from the μSR linewidth, since the superconducting contribution to the width is proportional to λ^{-2}. In Fig. 5 we compare measure-

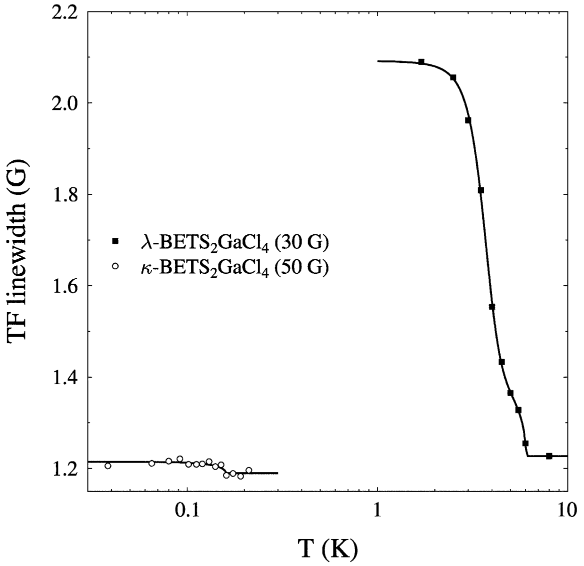

Fig. 4. TF linewidth against temperature for two different crystal phases of non-magnetic BETS$_2$GaCl$_4$ salt.

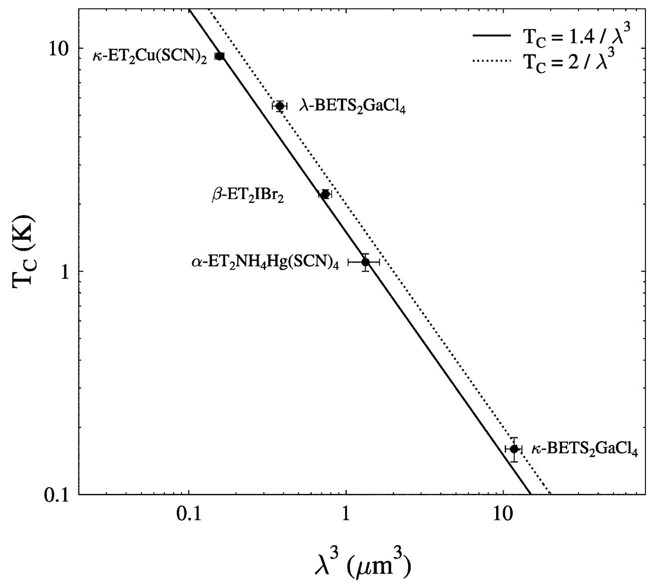

Fig. 5. Correlation between the superconducting transition temperature and the penetration depth parameters derived from this study and earlier muon studies [15] on a range of non-magnetic organic superconducors.

ments we have made on a variety of organic superconductors, combining the BETS salts in this study with some studies of ET salts reported earlier [15]. A strong correlation emerges between having small λ and high T_c. This type of correlation was pointed out earlier by Uemura in the context of underdoped cuprates and other 2D superconductors [16]. This Uemura scaling has T_c directly proportional to λ^{-2}, which is proportional to the 2D Bose–Einstein condensation temperature of a gas of preformed local pairs. However in the data here the observed T_c scaling follows λ^{-3} in the set of organic superconductors we have measured so far. This different scaling behavior may be the result of the conduction plane anisotropy, which is a common feature of all organic superconductors which have lower symmetry structures compared to the layered inorganic systems such as the cuprates.

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