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SUPERCONDUCTIVITY AT AMBIENT PRESSURE IN BEDT-TTF RADICAL SALTS

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ABSTRACT

Crystals of $(BEDT-TTF)_2Cu(NCS)_2$ were prepared by several methods and the superconducting transitions investigated by resistivity and ac susceptibility measurements. Depending on the preparation of the crystals a variation of the temperature of the superconducting transition is observed. This variation is manifested in the upper critical fields H_{C2} and proton NMR relaxation measurements at temperatures below T_C show it as well.

The upper critical fields H_{C2} of crystals of α_t-$(BEDT-TTF)_2I_3$ were determined in dependence of the temperature and of the direction of the magnetic field with respect to the various crystal axes by measuring the mid transition of the resistivity and of the rf penetration depth. The data are analyzed with the anisotropic effective mass model in the picture of the Ginsburg Landau (GL) theory as well as in the picture of a layered superconductor. ^{13}C Knight shifts measured by magic angle sample spinning and NMR cross polarisation methods support the picture of the layered superconductor.

INTRODUCTION

Recently two new ambient pressure organic superconductors with transition temperatures T_C at 8K and 10.4K were discovered. Both are radical salts of the donor bis(ethylenedithio)-tetrathiafulvalene (BEDT–TTF) prepared by electrochemical methods. The first superconductor – α_t-$(BEDT-TTF)_2I_3$ – is obtained by tempering crystals of α-$(BEDT-TTF)_2I_3$ for several days at a temperature around 75^0C [1,2]. This procedure leads to a phase transition. The new structure is similar to the one of β-$(BEDT-TTF)_2I_3$, but the crystals of α_t-$(BEDT-TTF)_2I_3$ have a transition into a stable superconducting state at 8K. It was shown [2] by measuring the ac susceptibility that the transition is rather broad, but at 1.3K a volume superconductivity of about 70% was observed.

Superconductivity at even 10.4K has recently been reported in $(BEDT-TTF)_2Cu(NCS)_2$ by Urayama et al. [3] and was confirmed by Gärtner et al. [4]. In contrast to other organic

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superconductors a relatively sharp superconducting transition even in the ac susceptibility is observed in (BEDT−TTF)$_2$Cu(NCS)$_2$ [4]. At 8K a diamagnetic shielding signal of at least 70% with respect to a perfect superconductor was found, indicating a strong bulk effect [4]. Nevertheless, by cooling crystals of (BEDT−TTF)$_2$Cu(NCS)$_2$ down from room temperature first an increase in resistivity until around 100K is observed [3,4], whereby the ratio ρ(100K)/ρ(300K) varies between 1.5 and 25 depending on the preparation of the crystals. On the other side thermopower measurements demonstrate the metallic character of the crystals in the whole temperature range below 300K, but indicate as well phase transitions at around 100K and 50K [4].

Here we report investigations of the resistivity, ac susceptibility, critical fields and proton NMR relaxation on (BEDT−TTF)$_2$Cu(NCS)$_2$ crystals, which were prepared under various conditions in the electrochemical syntheses. In addition the upper critical fields of α_t-(BEDT-TTF)$_2$I$_3$ crystals were determined and the data analyzed in the picture of a layered superconductor.

RESULTS AND DISCUSSION

(BEDT−TTF)$_2$Cu(NCS)$_2$

Crystals of (BEDT−TTF)$_2$Cu(NCS)$_2$ were first prepared by Urayama et al [3] using the crown ether route in the electrochemical preparation as first described by Geiser et al [5]. A similar preparation was used in [4], but instead of taking as electrolyte a mixture of CuSCN and K(18−crown−6)SCN we used the combination of CuSCN, KSCN and the 18−crown− 6ether. We have now synthesized crystals of (BEDT−TTF)$_2$Cu(NCS)$_2$ under various preparative conditions, first by using different solvents and second by varying the concentration of the 18−crown−6 ether in the solution. In addition we have used the mixture of CuSCN and (n−Bu$_4$N)SCN as described by Carlson et al [6] for preparing the crystals. Further we have used in some preparations deuterated BEDT−TTF.

Crystals from all batches were investigated by resistivity (1.3−300K) and ac susceptibility measurements, resulting in over 50 measurements of the temperature dependence of the resistivity of different (BEDT−TTF)$_2$Cu(NCS)$_2$ crystals. In every case the superconducting transition (T_c) was evaluated by taking the center of the resistive transition between the onset temperature and the temperature where the resistivity is zero. The "best" crystals with respect to crystal quality and sharpness of the superconducting transition were obtained by using 1,1,2− trichloroethane (TCE) as a solvent. In 100ml TCE at 50°C 70mg BEDT−TTF (1.8mmol), 122mg CuSCN (10mmol), 97mg KSCN (10mmol) and 265mg 18−crown−6 ether (10mmol) were dissolved. The solution with a remainder of undissolved CuSCN and KSCN was filled into the electrochemical cell. At 20°C and under constant voltage conditions with a current density of about 1μA/cm^2 the crystals were grown in about 8 days. The largest crystals obtained in this manner had the size of 10x2x0.1mm. The highest observed T_c was 10.8K (see fig.1), whereby the onset temperature is clearly above 11K and at 10K zero resistivity is found.

Crystals of similar size and quality were obtained in cases where the undissolved CuSCN and KSCN was filtered off before the electrochemical process was started but the super-

conducting transition seems to be broader even if the onset temperature is nearly the same. In addition the ESR linewidth at room temperature of these crystals is much broader (60–70 G as observed in [6,7]), while it is only 25 G in the first case (as reported in [4] and seen at low temperature as well by Urayama et al [7]). Nevertheless all crystals have the same structure and unit cell data.

With higher concentrations of 18–crown–6 ether and KSCN the crystals grow much faster but their quality is worse.

Crystals grown in other solvents like chlorobenzene or tetrahydrofurane have lower transition temperatures ($T_c \sim 8.0–9.5$ K) and the transitions are broader. The same observation was made with crystals prepared in TCE with a mixture of CuSCN and $(n-Bu_4N)SCN$ as electrolyte. In all cases the onset for the diamagnetic shielding in the ac susceptibility was observed at those temperatures where the resistivity becomes zero. Nevertheless, compared to all other known organic superconductors the transitions were always relatively sharp (see [4]) and in the best cases at 2K diamagnetic shielding signals of 95% with respect to a perfect superconductor were observed.

The "best" crystals prepared from deuterated BEDT–TTF showed an onset for superconductivity of 11.4 K and a mid transition of 11.1K, while zero resistivity was found at 10.4K (see fig. 1a, resistivity along the b–direction). Nevertheless, a comparison between the resistivity curves of the "best" protonated ("normal") and deuterated $(BEDT-TTF)_2Cu(NCS)_2$ crystals (fig. 1) shows a very similar transition for both types of crystals. The same is valid for "typical" crystals which have a similar onset temperature for superconductivity but show a broader transition as can be seen from fig. 1b. Again the resistivity characteristics are very similar. By investigating the upper critical fields H_{c2}, especially in the temperature range near the transition temperature, we found some differences between normal and deuterated crystals. Figs. 2a and b show the temperature dependences of H_{c2} with the magnetic field parallel to the a, b and c axes for normal and deuterated $(BEDT-TTF)_2Cu(NCS)_2$ crystals. In the case of the normal crystals H_{c2} shows no anisotropy for the magnetic field parallel to the b and c axes (fig. 2a) while for the deuterated crystals a difference in H_{c2} for both

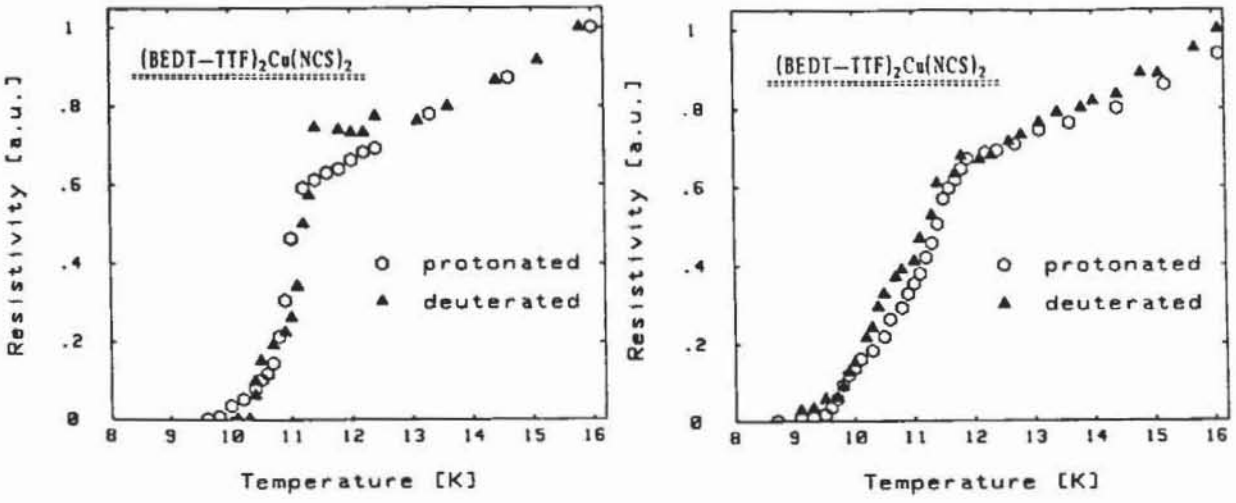

Fig. 1a. (left) resistivity(along the b axes) versus temperature of two of the "best"crystals of $(BEDT-TTF)_2Cu(NCS)_2$.

Fig. 1b. (right) resistivity versus temperature of "typical" crystals of $(BEDT\text{-}TTF)_2Cu(NCS)_2$.

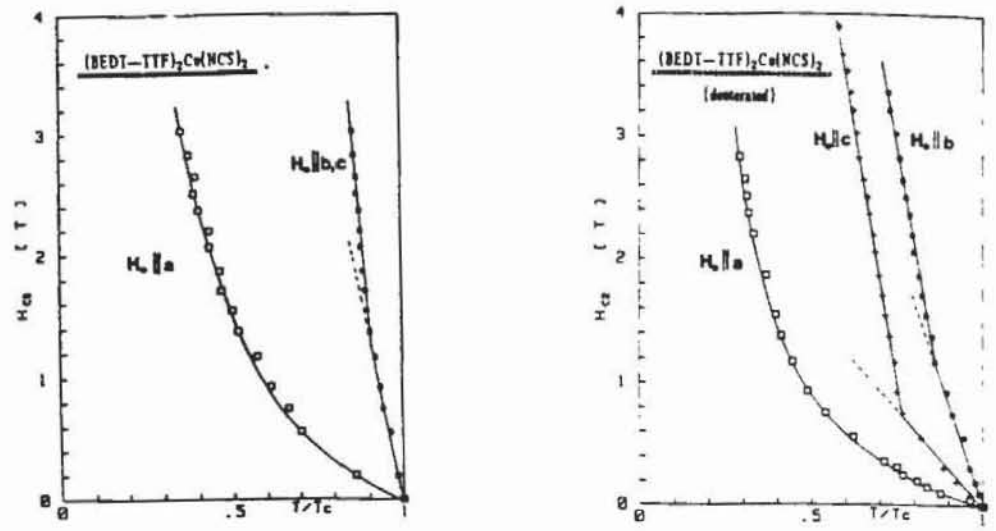

Fig. 2 Temperature dependence of the upper critical fields H_{c2} for the magnetic field parallel to the a, b and c axes for: a) (left) normal (BEDT-TTF)$_2$Cu(NCS)$_2$; b) (right) deuterated (BEDT-TTF)$_2$Cu(NCS)$_2$ crystals.

directions is found (Fig. 2b). Nevertheless, in both cases a clear crossover from an anisotropic three dimensional to a two dimensional behaviour is observed. A similar observation was already made by Oshima et al. [8] for the normal crystals.

On the other hand the upper critical fields H_{c2} depend on the quality, that means on the preparation of the crystals. This is demonstrated by proton relaxation measurements at low temperatures on two different batches of crystals. In the case of β-(BEDT-TTF)$_2$I$_3$ [9] it was first demonstrated that in the two dimensional organic superconductors a striking enhancement of the proton spin lattice relaxation rate T_1^{-1} occurs at the critical temperature $T_c(H,H_{c2})$. Here H is the applied magnetic field and H_{c2} is the lowest value of the anisotropic upper critical fields.

This behaviour of the spin lattice relaxation rate was attributed [9] to a logarithmic critical singularity whose amplitude is enhanced by the low dimensional character of these conductors.

In (BEDT–TTF)$_2$Cu(NCS)$_2$ a similar striking enhancement of the proton relaxation rate was observed [10, 11]. The maximum of the enhancement depends strongly on the quality of the crystals. This is demonstrated in fig. 3a where the temperature dependence of the proton relaxation rates T_1^{-1} measured at a magnetic field of 0.33 T for two different batches of (BEDT–TTF)$_2$Cu(NCS)$_2$ crystals are shown. In the case of the "better" batch the maximum is found at 5.2 K while in the second case the maximum appears at 4 K (as observed in [11] as well). The batch with the higher critical temperature at the field of 0.33 T has a somewhat smaller enhancement of the relaxation rate. This is probably due to the fact that at 5.2 K the crossover from the anisotropic three dimensional to the two dimensional behaviour (as demonstrated in fig. 2) is not totally fulfilled. Since the enhancement depends strongly on the low dimensional character [9] the enhancement in the "better" batch with the critical temperature of 5.2 K at 0.33 T is smaller. This agrees with the finding in the 8 K superconductor α_t-(BEDT-TTF)$_2$I$_3$ where only a weak enhancement of the proton

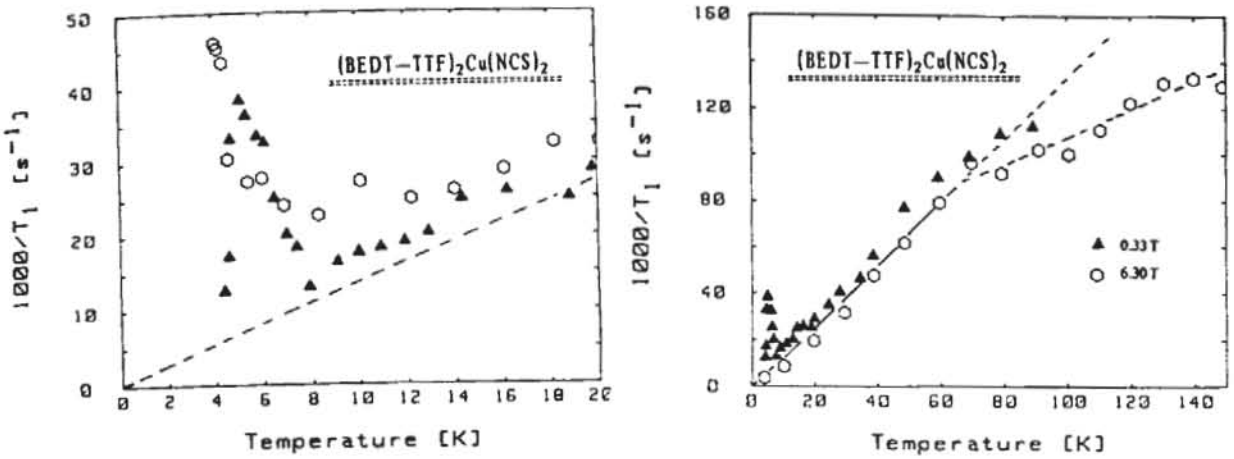

Fig. 3a. (left) Proton relaxation rates T_1^{-1} at a magnetic field of 0.33T for two different batches of $(BEDT-TTF)_2Cu(NCS)_2$ crystals at low temperatures.
Fig. 3b. Temperature dependence of the proton relaxation rates of $(BEDT-TTF)_2Cu(NCS)_2$ at the magnetic fields of 0.33T and 6.3T.

relaxation rates was observed [10] and where at this magnetic field a clear three dimensional character prevails as will be shown later. In fig. 3b the proton relaxation rates T_1^{-1} of the "better" batch up to 140K for 0.33T and 6.3T are shown. The relaxation rates between 20K and 60K are very similar for both fields. Those for the smaller field seem to be a little larger. Above 140K the relaxation rates at 6.3T increase rapidly (at the lower field already above 100K) due to a fast flipping of the CH_2 –groups of the BEDT–TTF molecules. Below 60K the Korringa relation $T_1 \cdot T = \text{const.} = 7.3 \cdot 10^2$ sec·K is fulfilled. Above 60K the relaxation rates at 6.3T are smaller than predicted by the Korringa law at low temperatures. The break at around 60K is probably due to a metal metal phase transition, which was observed earlier in thermopower [4] and susceptibility [12] measurements. A detailed discussion of the NMR data will be given elsewhere [13].

α_t-(BEDT-TTF)$_2$I$_3$

Crystals of α_t-$(BEDT-TTF)_2I_3$ were prepared by tempering α-$(BEDT-TTF)_2I_3$ [2]. α-$(BEDT-TTF)_2I_3$ is an organic metal at temperatures above 135K [14]. At 135K a metal insulator phase transition occurs. The tempering procedure leads to a phase transition. The α_t- phase has a unit cell and structure which is very similar to the one of β-$(BEDT-TTF)_2I_3$ as was shown by ESR–, thermopower–, NMR– and Raman investigations [2]. Nevertheless, the exact structure is not known yet, due to the fact that during the phase transition at 75°C only small parts of the size of some μm^3 stay as single crystals, although the macroscopic crystal is still mechanically stable. This fact can be observed for thin crystals under a polarisation microscope. As a result of this type of phase transition the α_t–$(BEDT-TTF)_2I_3$ crystals behave as hard superconductors. The upper critical fields $H_{c2\perp} = 2.15$T for the magnetic field perpendicular to the ab-plane and $H_{c2\parallel} = 12$T for the magnetic field parallel to the ab-plane [15] are much higher than those of β-$(BEDT-TTF)_2I_3$ in the metastable 8K superconducting state [16]. Fig. 4a shows the angular dependence of H_{c2} of α_t-$(BEDT-TTF)_2I_3$ [15].

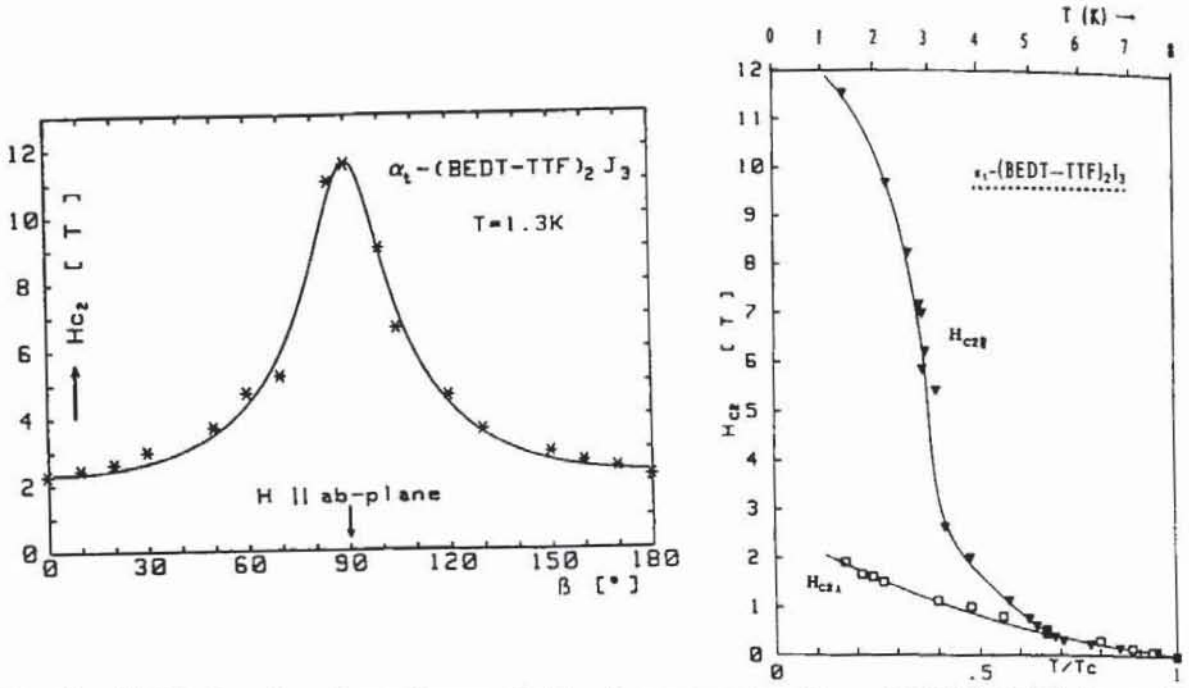

Fig. 4a. (left) Angular dependence of H_{c2} for crystals of α_t-(BEDT-TTF)$_2$I$_3$ at 1.3K.
Fig. 4b. (right) Temperature dependence of H_{c2} for crystals of α_t-(BEDT-TTF)$_2$I$_3$ for the magnetic field perpendicular ($H_{c2\perp}$) and parallel ($H_{c2\|}$) to the ab-plane.

In addition the temperature dependence of the upper critical fields $H_{c2\perp}$ and $H_{c2\|}$ are shown in fig. 4b. It can clearly be seen that for the region $T/T_c > 0.65$ (T_c=8K) the crystals behave as isotropic three dimensional superconductors, since for all directions the upper critical fields are the same. In the region $0.45 < T/T_c < 0.65$ an anisotropic three dimensional

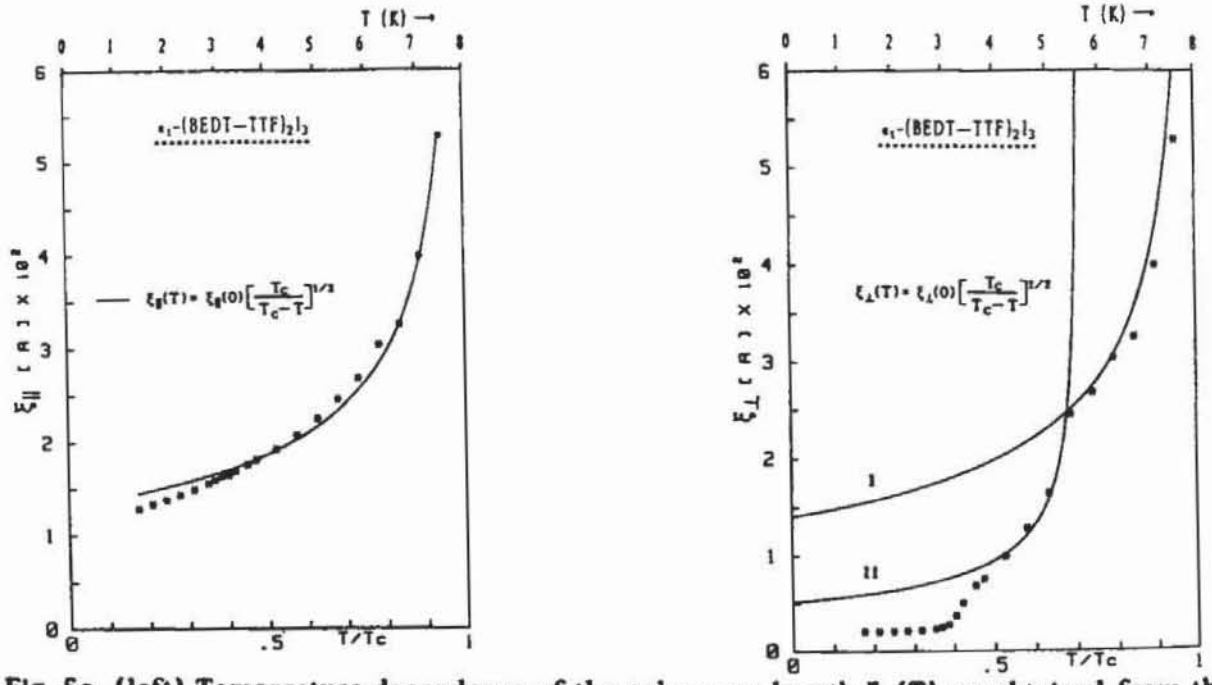

Fig. 5a. (left) Temperature dependence of the coherence length $\xi_{\|}(T)$ as obtained from the data in fig. 4b and applying the anisotropic GL theorie for α_t-(BEDT-TTF)$_2$I$_3$ (coherence length in the ab-plane).
Fig. 5b. (right) Same for $\xi_{\perp}(T)$ (coherence length perpendicular to the ab-plane).

behaviour is found. For $T/T_c < 0.45$ the system can be described in the picture of a typical two dimensional layered superconductor [17].

The analysis was done in the following way. First, using the data of fig. 4b and applying the anisotropic effective mass model of the GL theory we calculated the coherence length $\xi_{\parallel}(T)$ and $\xi_{\perp}(T)$ from equations (1) and (2).

$$(1) \qquad \xi_{\parallel}(T)=\left[\frac{\Phi_o}{2\pi\mu_o H_{c2\perp}(T)}\right]^{1/2}; \qquad \xi_{\perp}(T)=\left[\frac{\Phi_o H_{c2\perp}(T)}{2\pi\mu_o H^2_{c2\parallel}(T)}\right]^{1/2} \qquad (2)$$

with Φ_0 the flux quantum. The values for the coherence lengths $\xi_{\parallel}(T)$ and $\xi_{\perp}(T)$ are shown in fig. 5a and b (crosses). The values $\xi_{\parallel}(T)$ and $\xi_{\perp}(T)$ so obtained, were fitted to the equations (3) and (4)

$$(3) \qquad \xi_{\parallel}(T)=\xi_{\parallel}(0)\left[\frac{T_c}{T_c-T}\right]^{1/2} \quad ; \qquad \xi_{\perp}(T)=\xi_{\perp}(0)\left[\frac{T_c}{T_c-T}\right]^{1/2} \quad ; \quad (4)$$

resulting in the solid curves in figs. 5a,b. In eqs. 3 and 4 $\xi_{\parallel}(0)$ and $\xi_{\perp}(0)$ are adjustable parameters. In ref. [15] a value $\xi_{\parallel}(0)=123$A was obtained from eq. 1 by extrapolating to T=0K. The coherence length $\xi_{\parallel}(T)$ can be described in the whole temperature range quite well by the anisotropic three dimensional GL theory (see fig. 5a).

In contrast, the coherence length $\xi_{\perp}(T)$ has to be described in a different manner. The solid curve I in fig. 5b is a fit for an isotropic three dimensional case, while curve II represents the fit within the anisotropic three dimensional GL picture. Here T_c must be replaced by $T_c^* = T_c \cdot 0.65$ where T_c^* corresponds to the crossover temperature from the isotropic to anisotropic three dimensional behaviour.

The region $T/T_c < 0.45$ can be described within the framework of two dimensional superconductors coupled by electron tunneling between adjacent layers [17]. In the picture of the anisotropic GL theory $\xi_{\perp}(0) = 22$A was obtained [15]. However, since the anisotropic GL theory is only valid sufficiently close to T_c such that the GL coherence length perpendicular to the layers $\xi_{\perp}$ is much larger than the layer separation, it is not expected to be correct at low temperatures where $\xi_{\perp}(0)$ should become less or comparable to the layer separation. Nevertheless, the 22A are comparable to the unit cell dimension in the c-direction. On the other hand this value is still larger than the distance between the conducting cationic BEDT–TTF planes. This means that the thicknes of the superconducting layers has to be smaller than the thickness of the BEDT-TTF layers. This picture is supported by results of ^{13}C Knight shift measurements [10,13] which were obtained on ^{13}C enriched samples by magic angle sample spinning and NMR cross polarization methods. The obtained Knight shifts for the carbons of the BEDT-TTF molecules in α_t-(BEDT-TTF)$_2$I$_3$ are 125 and 92 ppm respectively for the inner carbons, 62, 51, 44 and 24 ppm for the middle carbons and 5.5, -6.7, -7.3 and -9.7 ppm for the outer carbons. Since the size of the Knight shifts is a measure for the spin densities (and therefore to some degree for the charge densities as well) we conclude that the conduction electrons are mainly located on the middle part of the BEDT-TTF molecules. From this follows that the thickness of the superconducting layer is of the order of 6 to 10A supporting nicely the picture of the Josephson coupled two dimensional layered superconductors as described by Klemm et al [17].

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