TEMPERATURE AND ANGULAR DEPENDENCE OF THE UPPER CRITICAL FIELD IN $\beta$-(BEDT-TTF)$_2$I$_3$ AND ITS DEUTERATED ANALOGUE

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We present measurements of the temperature and angular dependence of the upper critical fields of $\beta$-ET$_2$I$_3$ and d-$\beta$-ET$_2$I$_3$. The data are analyzed in terms of an anisotropic effective mass model. The results of cooling rate experiments are reported and the effect of deuteration on superconductivity is discussed.

1. INTRODUCTION

$\beta$-(BEDT-TTF)$_2$I$_3$ (or $\beta$-ET$_2$I$_3$, for short) is the prototype of a new family of ambient pressure organic superconductors /1/. It has recently attracted considerable interest because of a high-\(T_c\) state that can be obtained under a soft pressure /2-4/ and, after previous pressurization, even at ambient pressure /5,6/. The purpose of this paper is to better characterize the superconducting ground state of $\beta$-ET$_2$I$_3$ in its pristine form by determining the anisotropy of the upper critical fields as well as to investigate the effects of substitution of the H-atoms in the ET molecule by deuterium and the effects of cooling rate.

2. EXPERIMENTAL

Single crystals of the title compound were grown by the usual electrochemical method, identified by their characteristic distorted-hexagon shape and picked from the mixture of $\alpha$- and $\beta$-phase crystals that constituted the usual product of electrolysis. The directions of the crystallographic axes relative to the macroscopic crystals were determined by measuring the angles formed by the crystal edges. The samples were then inserted into the tank coil of a tunnel diode oscillator such that the stacking axis ([110] direction) was parallel to the a.c. field. A device attached to the evaporation chamber of a $^3$He cryostat allowed the coil assembly to be rotated relative to the magnetic field at low temperatures. This contactless technique was chosen primarily in order not to apply shear to the sample due to differential thermal contraction of the sample and the contact material. A plot of the oscillator's frequency change versus temperature served to determine $T_c$, defined as linearly extrapolated onset of the transition as a function of magnetic field.

3. RESULTS

In both of the title compounds the upper critical fields essentially show a linear variation with temperature, with a tendency towards a upward curvature in $\beta$-ET$_2$I$_3$ and downward curvature in d-$\beta$-ET$_2$I$_3$. A linear extrapolation to \(T = 0\) gives values that are close to the paramagnetic limit \(H_p = 18.4 \cdot T_c\) kG/K for directions parallel and perpendicular to the stack, whereas the critical fields in \(c^\star\)-direction are lower by a factor of about twenty (see fig. 1 and 2 and table 1 for numerical values). Fig. 3 shows a plot of the angular dependence of \(H_{c2}\) in one sample of $\beta$-ET$_2$I$_3$ at 0.8 K. The solid line re-
Fig. 1: Temperature dependence of $H_{c2}$ in $\beta$-ET$_2$I$_3$, normalized to the paramagnetic limit: $H_p = 18.4 \cdot T_c$ kG/K. Solid lines are to guide the eye.

Fig. 2: Temperature dependence of $H_{c2}$ in d-$\beta$-ET$_2$I$_3$, normalized to the paramagnetic limit.

A striking feature of the data for d-$\beta$-ET$_2$ is that its $T_c$ is noticeably higher than that of the protonated material in contrast to what one would expect from a simple BCS approach or from the known pressure effect, namely a depression of $T_c$.

$\beta$-ET$_2$I$_3$ is reported to exhibit a structural phase transition below 200 K /7,8/, the suppression of which is believed to give rise to the material's high-$T_c$-state /6/. We have investigated the influence of the cooling rate in the following manner: In order to freeze in any left over traces of the high temperature phase the sample was slowly heated to the highest achievable temperature of around 100 K and then cooled back to helium temperature in 6 - 8 minutes by introducing He exchange gas into the vacuum can of the cryostat. This procedure resulted in a decrease of the transition temperature of 0.1 and 0.08 K for $\beta$-ET$_2$I$_3$ and d-$\beta$-ET$_2$I$_3$ respectively. After subsequent annealing and

Table I: Measured and derived superconducting properties of $\beta$-ET$_2$I$_3$ and d-$\beta$-ET$_2$I$_3$

<table>
<thead>
<tr>
<th>material</th>
<th>$H_{c2}(0)$ [kG]</th>
<th>$\xi_{GL}$ [$\AA$]</th>
<th>$T_c$ /$T_\perp$</th>
<th>$m_\parallel / m_*$</th>
<th>$T_c$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-ET$_2$I$_3$</td>
<td>20.9</td>
<td>587</td>
<td>1.28</td>
<td>1.40</td>
<td>1.15</td>
</tr>
<tr>
<td>H stack</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L stack</td>
<td>24.8</td>
<td>696</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_{c2}$</td>
<td>0.806</td>
<td>22.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-$\beta$-ET$_2$I$_3$</td>
<td>25.8</td>
<td>506</td>
<td>1.75</td>
<td>1.02</td>
<td>1.43</td>
</tr>
<tr>
<td>H stack</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L stack</td>
<td>25.5</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_{c2}$</td>
<td>1.30</td>
<td>25.5</td>
<td></td>
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</tr>
</tbody>
</table>
slow cooling the transition temperatures are partly recovered. No traces of the high-$T_c$-state, however, could be detected.

4. DISCUSSION

As can be seen on Fig. 3 it is difficult to tell from the angular dependence data whether a thin film or a three dimensional, though anisotropic, description of this layered material is more appropriate. As in the temperature dependence data a clear cut evidence for thin film behaviour, such as an upturn due to decoupling of the layers, is lacking, we adopt an anisotropic Ginzburg-Landau-model, in which the expression for $H_{c2}$ takes the form

$$H_{c2i} = \phi_0 / 2\pi \xi_j \xi_k, \quad i, j, k = \|, \perp, \text{stack, } \perp \text{c}$$

($\phi_0$: flux quantum, $\xi_i$: GL coherence length). Assuming coherent transport in the ab plane, the coherence lengths may be used to estimate the corresponding transfer integrals $t_i$ by using $(d_{\|}, d_{\perp}$: repeat distances along and perpendicular to the stack). With these values (see tab. I) the bandstructure of the title compounds is established to be quasi-twodimensional with a closed Fermi surface in the ab plane.

As to the isotope effect, we note that the observed difference in $T_c$ is still within the range of $T_c$ in $\beta$-ET$_2$I$_3$ that is reported by various different authors (1.1 - 1.6 K). This large spread is probably due to minute differences in crystal composition due to the complicated electrochemistry of the ET-iodine system. We are, however, confident that the isotope effect is real since great care was taken to assure equal crystallization conditions and the difference exceeds the usual scatter from batch to batch.

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REFERENCES

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