MICROWAVE HALL MOBILITY AND CONDUCTIVITY IN CRYSTALS OF VARIOUS (BEDT-TTF) RADICAL SALTS

M. DRESSEL* and H.W. HELBERG
Drittes Physikalisches Institut der Universität Göttingen, Göttingen (F.R.G.)
D. SCHWEITZER
Drittes Physikalisches Institut der Universität Stuttgart, Stuttgart (F.R.G.)

ABSTRACT

We report investigations of the microwave transport properties carried out on the organic conductors and superconductors of (BEDT-TTF)-salts: α-, ακ- and β-(BEDT-TTF)$_2$I$_3$, α-(BEDT-TTF)$_3$(NO$_3$)$_2$ and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The anisotropy and temperature dependence (300 K to 4 K) of the high-frequency conductivity was measured in a microwave cavity at 10.3 GHz. There is low anisotropy in the high conducting plane of the quasi two-dimensional crystals of the (BEDT-TTF)-family, e.g. the $a_b$-plane in β-(BEDT-TTF)$_2$I$_3$; perpendicular to this the microwave conductivity is one order of magnitude lower. At room temperature the microwave Hall mobility at 9.5 GHz of the different phases of (BEDT-TTF)$_2$I$_3$ and (BEDT-TTF)$_3$(NO$_3$)$_2$ is 100 to 200 cm$^2$/Vs in the high conducting planes of the crystals. With about 1200 cm$^2$/Vs the high-frequency mobility of the superconductor (BEDT-TTF)$_2$Cu(NCS)$_2$ is similar to the one measured in the $a_b$-plane of the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$.

INTRODUCTION

Due to small size and uncertainty of the contact resistance at single crystals of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) radical salts the dc-Hall measurements are very difficult [1, 21. Contactless high-frequency methods for studying the bulk transport properties of (BEDT-TTF) crystals were used to avoid the problems affected by various surface effects: the cavity perturbation technique for measuring the ac-conductivity and bimodal cavities suitable for the determination of the Hall mobility in very small crystals.

EXPERIMENTAL TECHNIQUES

All microwave investigations were performed at small crystalline samples (e.g. 1 mm x 0.05 mm). The samples were placed in the centre of a cylindrical cavity working in the TE$_{111}$ or TM$_{010}$-mode at 10.3 GHz for conductivity measurements. The complex permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ and thus the conductivity $\sigma$ is determined from the frequency shift and the change of the quality factor, using the well-known cavity perturbation technique [3].

In order to measure the microwave Hall mobility $\mu_H$ we used bimodal cavities of different shape, size and frequency [4], e.g. a cylindrical TE$_{112}$-cavity for 9.5 GHz, similar to the one described by Ong, Bauhofer and Wei [5]. Iris coupling of two orthogonal waveguides was chosen instead of probe coupling [6] for greater mechanical stability. In one antinode of the orthogon-
nal electric fields a flat sample was placed in such a way as to allow the current paths to be in the sample plane. With the help of four tuning probes and two iris tuner we were able to obtain a mode separation of 65 dB up to 80 dB depending on the shape of the sample. The procedure of balancing the cavity is described in Ref. [4 – 7]. Using a bucking channel (1) as shown in Fig. 1 the remaining non-ideal output signal could be cancelled below the apparatus limit (-100 dBm) of the superheterodyne receiver (SR). For keeping the shf-generator (G) precisely at the resonant frequency of the cavity a special frequency control (FC) was used. After tuning the cavity the degeneration of the two modes was better than 200 kHz. The static magnetic field ($B < 1$ Tesla) was applied normal to the sample surface, i.e. parallel to the axis of the cavity, and induced a rotation of the current paths in the sample by the Hall angle $H = \arctan(\mu_H B)$. The analysis of the dual mode cavity by a scattering matrix $S$ [4, 6, 8] leads to

$$\tan \theta_H = \mu_H B = \frac{-1}{f(S) g(S)} \sqrt{\frac{P_o}{P_i}},$$

(1)

with $P_i$ and $P_o$ the input power, resp. output power; $f(S)$ is a function of the permittivity $\varepsilon'$, $\varepsilon''$ and the depolarization factor $Q$ of the sample and becomes exactly 1 for low conductivity and $f(S) = -1$ for high conductivity [4, 9]: $N \varepsilon'' = 1 + N \varepsilon'' - 1$. By measuring the reflection coefficient of the loaded cavity at each waveguide ($I_{S1}$ resp. $I_{S2}$) and the quality $Q_S$ and $Q_o$ of the loaded and unloaded cavity the factor $g(S)$ can be determined in the symmetrical case [4, 6, 8]:

$$g(S) = \left(1 - \frac{Q_S}{Q_o}\right) \sqrt{(1 - I_{S1})(1 - I_{S2})}.$$  

(2)

The transmitted signal is proportional to $\mu_H B$ for weak magnetic field [6, 8, 10]. It could be determined by using a variable calibrated attenuator (PA1) and a phase shifter (P) for zero adjustment. The apparatus was tested with p-GaAs and the accuracy is about 20%. A detailed discussion of the experimental errors and accuracy can be found in Ref. [4, 11]. The influence of the depolarization factor [4, 9], the Hall effect in the cavity walls (Lorentz force on the wall current) [11 – 12] and the effects of the second and third order in $B$ (e.g. influence of the magnetoresistance) [8] were taken into account in the advanced data analysis [4].

RESULTS AND DISCUSSION

Above the phase transition at $T_{MI} = 135$ K the microwave conductivity of $\alpha$-(BEDT-TTF)$_2$I$_3$ is rather constant and isotropic with a room temperature value of 30 (Ωcm)$^{-1}$ in the high con-
ducting (α,β)-plane [13]. Tempering a sample for a few days at 70°C it undergoes a transition to the superconducting α-Phase (Tc = 8 K) [14]. In α-(BEDT-TTF)2I3 the metal-isolator transition is suppressed and the conductivity is quite constant down to 4 K (Fig. 2). The microwave conductivity at 10.3 GHz in the (α,β)-plane of the former α-phase is about 20 (Ωcm)-1 at room temperature. The related β-modification undergoes a number of phase transitions and sub-phases between 300 and 4 K. Different β-(BEDT-TTF)2I3-crystals show no unique temperature behaviour of the microwave conductivity, depending on the crystal quality and history. The typical anisotropy of the high-frequency conductivity is shown in Fig. 3: \( \sigma_{ab}/\sigma_{xx} = 70 \).

In the crystals of (BEDT-TTF)2I3 we found no significant magnetoresistance in the whole temperature range from 300 K down to 4 K and for an applied magnetic field up to 1 Tesla. The maximum value for the magnetoresistance of α-(BEDT-TTF)2I3 reported by Pokhodyna et al. [11], is about two orders of magnitude below our apparatus limit of \( \Delta \rho = 10^{-2} \).

Investigations of the microwave Hall mobility could only be carried out at room temperature. The results for different crystals and orientations are listed in Table 1. The high-frequency Hall mobility is about 200 cm²/Vs for all modifications of (BEDT-TTF)2I3. The carrier mobility of α-(BEDT-TTF)2I3 might be affected by grain boundaries and remaining areas of the original α-phase. Assuming just one kind of charge carriers in α-(BEDT-TTF)I3 the Hall coefficient at room temperature would be estimated to \( R_H = \sigma/H = 8 \times 10^{-6} \text{ m}^2/\text{A}s \) and the charge carrier concentration \( n = \sigma/\mu H = 1 \times 10^{18} \text{ cm}^{-3} \), in contrast to optical studies [15] and thermoelectric measurements [13]. Therefore the high-frequency results can not be explained by a simple model with extended states-charge carriers. Our experimental data confirm the assumption of the existence of additional charge carriers generated by a narrow band near the Fermi level. These states were postulated by calculations of the electronic band structure [16]. They have to be characterized by low charge carrier density and high mobility.

In (BEDT-TTF)3(NO3)2 the hf-conductivity is ranging from 100 to 350 (Ωcm)-1, depending on the quality of the crystals. The results for the Hall mobility \( \mu_H \) (T = 300 K) = 120 cm²/Vs and the carrier concentration \( n = 2 \times 10^{19} \text{ cm}^{-3} \) are in good agreement with the characterisation as a semiconductor. The large mobility 1200 cm²/Vs in (BEDT-TTF)2Cu(NCS)2 corresponds to a high microwave conductivity of about 400 (Ωcm)-1 at 300 K. In crystals of the high-\( T_c \) superconductor YBa2Cu3O7, values of the same order were measured: \( \mu_H = 1900 \text{ cm}^2/\text{Vs} \).

The high-frequency measurements have to be continued in order to get a better character-

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**Fig. 2.** Temperature dependence of the microwave conductivity of α-(BEDT-TTF)2I3 measured at a frequency of 10.3 GHz in the (α,β)-plane of the former α-phase.

**Fig. 3.** Microwave conductivity at 10.3 GHz in a single β-(BEDT-TTF)2I3-crystal versus temperature for three crystal directions: (+) in the (α,β)-plane perpendicular to the chain; (a) parallel to the chain; (□) normal to the (α,β)-plane.
**TABLE 1**

Microwave Hall mobility measured in a bimodal cavity at 9.5 GHz and 300 K for different samples and crystal orientations with an applied magnetic field \( B \) up to 0.8 Tesla.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Microwave Hall mobility</th>
<th>Orientation of the electrical field</th>
<th>Orientation of the magnetic field</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha-(\text{BEDT-TTF})_2\text{I}_3 )</td>
<td>250 cm(^2)/Vs</td>
<td>in ((\overline{a},\overline{b}))–plane</td>
<td>( \parallel \overline{c} ) *</td>
</tr>
<tr>
<td>( \beta-(\text{BEDT-TTF})_2\text{I}_3 )</td>
<td>200 cm(^2)/Vs</td>
<td>in ((\overline{a},\overline{b}))–plane</td>
<td>( \parallel \overline{c} ) *</td>
</tr>
<tr>
<td>( \alpha_-\text{I}_{3} )</td>
<td>160 cm(^2)/Vs</td>
<td>in ((\overline{a},\overline{c}))–plane</td>
<td>( \parallel \text{in (001) } \perp \overline{a} )</td>
</tr>
<tr>
<td>( \alpha-(\text{BEDT-TTF})_3(\text{NO}_3)_2 )</td>
<td>120 cm(^2)/Vs</td>
<td>in ((\overline{a},\overline{c}))–plane of the original ( \alpha )-phase</td>
<td>( \parallel \overline{c} ) *</td>
</tr>
<tr>
<td>( x-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 )</td>
<td>1200 cm(^2)/Vs</td>
<td>in ((\overline{a},\overline{c}))–plane</td>
<td>( \parallel \overline{a} ) *</td>
</tr>
<tr>
<td>( \text{YBa}_2\text{Cu}_3\text{O}_7 )</td>
<td>1900 cm(^2)/Vs</td>
<td>in ((\overline{a},\overline{b}))–plane</td>
<td>( \parallel \overline{a} )</td>
</tr>
</tbody>
</table>

\* quantization of these materials. At the present stage it is difficult to find a quantitative description of the observed phenomena. For the definitive answer the frequency dependent conductivity and temperature dependent microwave Hall mobility measurements are planned.

**ACKNOWLEDGEMENTS**

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**REFERENCES**