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

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ABSTRACT

We report investigations of the microwave transport properties carried out on the organic conductors and superconductors of (BEDT-TTF)-salts: α-, α_t- 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 $(\vec{a},\vec{b})$-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 $(\vec{a},\vec{b})$-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, 2]. 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 × 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 σ 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 μ_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 orthogo-

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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 seperation 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 ($B \leq 1$ 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 arctan($\mu_H B$). The analysis of the dual mode cavity by a scattering matrix *S* [4, 6, 8] leads to

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

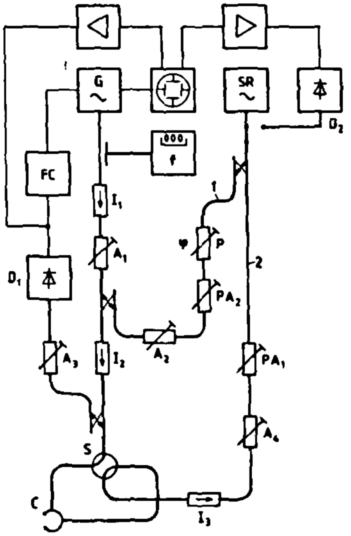
with P_i and P_o the input power, resp. output power; *f(S)* is a function of the permittivity ε', ε'' and the depolarization factor *N* of the sample and becomes exactly 1 for low conductivity and $f(S) = -1$ for high conductivity [4, 9]: $N\varepsilon'' \gg 1 + N(\varepsilon' - 1)$. By measuring the reflection coefficient of the loaded cavity at each waveguide (Γ_{S1} resp. Γ_{S2}) and the quality Q_S and Q_0 of the loaded and unloaded cavity the factor *g(S)* can be determined in the symmetrical case [4, 6, 8]:

$$g(S) = \left(1 - \frac{Q_S}{Q_0}\right) \sqrt{(1 - \Gamma_{S1})(1 - \Gamma_{S2})} \tag{2}$$

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 attentuator (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 α-(BEDT-TTF)$_2$I$_3$ is rather constant and isotropic with a room temperature value of 30 $(\Omega cm)^{-1}$ in the high con-



1	bucking and reference arm
2	main channel
G	microwave generator
f	frequency counter
FC	frequency control
SR	superheterodyne receiver
D	microwave diode
I	isolator
A	variable attenuator
PA	calibrated precision attenuator
P	variable phase shifter
S	waveguide switch
C	bimodal cavity

Fig. 1. Block diagram of the miocrowave circuit used for the dual mode cavity

ducting $(\vec{a},\vec{b})$-plane [13]. Tempering a sample for a few days at 70°C it undergoes a transition to the superconducting α_t-phase (T_c = 8 K) [14]. In α_t-(BEDT-TTF)$_2$I$_3$ 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 $(\vec{a},\vec{b})$-plane of the former α-phase is about 20 $(\Omega\mathrm{cm})^{-1}$ at room temperature. The related β-modification undergoes a number of phase transitions and subphases between 300 and 4 K. Different β-(BEDT-TTF)$_2$I$_3$-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: $\sigma_{ab}/\sigma_{c*} = 70$.

In the crystals of (BEDT-TTF)$_2$I$_3$ 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)$_2$I$_3$ reported by *Pokhodyna et. al.* [1], is about two orders of magnitude below our apparatus limit of $\frac{\Delta\rho}{\rho} = 10^{-2}$.

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 cm^2/Vs for all modifications of (BEDT-TTF)$_2$I$_3$. The carrier mobility of α_t-(BEDT-TTF)$_2$I$_3$ 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)$_2$I$_3$ the Hall coefficient at room temperature would be estimated to $R_H = \sigma/\mu_H = 8\cdot10^{-6}$ m^3/As and the charge carrier concentration $n = \sigma/\mu_H e = 1\cdot10^{18}$ 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 charriers 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)$_3$(NO$_3$)$_2$ the hf-conductivity is ranging from 100 to 350 $(\Omega\mathrm{cm})^{-1}$, depending on the quality of the crystals. The results for the Hall mobility μ_H (T = 300 K) = 120 cm^2/Vs and the carrier concentration $n = 2\cdot10^{19}$ cm^{-3} are in good agreement with the characterisation as a semiconductor. The large mobility 1200 cm^2/Vs in (BEDT-TTF)$_2$Cu(NCS)$_2$ corresponds to a high microwave conductivity of about 400 $(\Omega\mathrm{cm})^{-1}$ at 300 K. In crystals of the high-T_c superconductor YBa$_2$Cu$_3$O$_7$ values of the same order were measured: μ_H = 1900 cm^2/Vs.

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

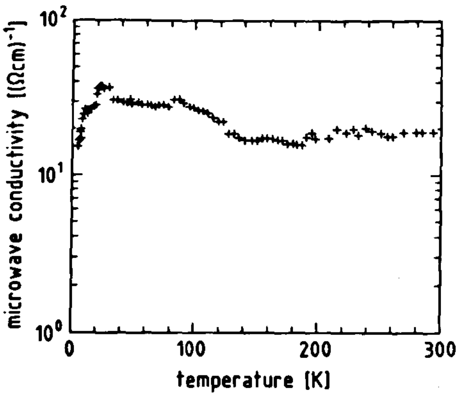


Fig. 2. Temperature dependence of the microwave conductivity of α_t-(BEDT-TTF)$_2$I$_3$ measured at a frequency of 10.3 GHz in the $(\vec{a},\vec{b})$-plane of the former α-phase

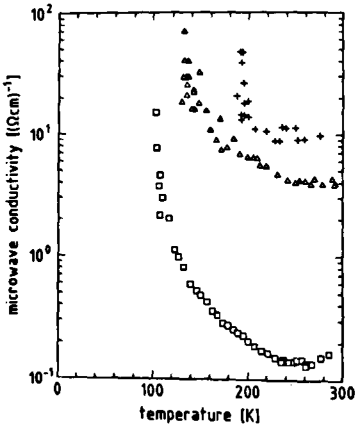


Fig. 3. Microwave conductivity at 10.3 GHz in a single β-(BEDT-TTF)$_2$I$_3$-crystal vesus temperature for three crystal directions : (+) in the $(\vec{a},\vec{b})$-plane perpendicular to the chain; (△) parallel to the chain; (□) normal to the $(\vec{a},\vec{b})$-plane

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.

Crystal	Microwave Hall mobility	Orientation of the electrical field	Orientation of the magnetic field
α-(BEDT-TTF)$_2$I$_3$	250 cm^2/Vs	in $(\vec{a},\vec{b})$-plane	$\vec{B} \parallel \vec{c}^*$
β-(BEDT-TTF)$_2$I$_3$	200 cm^2/Vs	in $(\vec{a},\vec{b})$-plane	$\vec{B} \parallel \vec{c}^*$
	160 cm^2/Vs	in $(\vec{a},\vec{c}^*)$-plane	$\vec{B}$ in (001) $\perp \vec{a}$
α_t-(BEDT-TTF)$_2$I$_3$	100 - 230 cm^2/Vs	in $(\vec{a},\vec{b})$-plane	$\vec{B} \parallel \vec{c}^*$
		of the original α-phase	
α-(BEDT-TTF)$_3$(NO$_3$)$_2$	120 cm^2/Vs	in $(\vec{a},\vec{c})$-plane	$\vec{B} \parallel \vec{b}$
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$	1200 cm^2/Vs	in $(\vec{b},\vec{c})$-plane	$\vec{B} \parallel \vec{a}^*$
YBa$_2$Cu$_3$O$_7$	1900 cm^2/Vs	in $(\vec{a},\vec{b})$-plane	$\vec{B} \parallel \vec{c}$

ization 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.

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