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Investigations of Organic Conductors by the Schegolev Method

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Abstract. — The Schegolev method is a well established technique to determine the dielectric properties of organic materials by placing the small samples in a microwave cavity and measuring the perturbation. The electronic properties can be studied without applying contacts and the frequency dependence gives information on the transport mechanism. The versatility of this unique method is reviewed by highlighting various applications on organic conductors and semiconductors.

1. Introduction

In the late sixties and early seventies the development of low dimensional organic conductors and semiconductors reached a new level and finally led to the synthesis of TTF-TCNQ. The fragility and limited size of the crystals, as well as high anisotropy caused major problems in characterizing their transport properties. At different laboratories a new measurement technique was developed which allows for a contactless determination of the complex conductivity by placing the specimen in a microwave cavity [1,2]. Although similar methods have been used for the characterization of conventional dielectric, ferroelectric, and magnetic materials [3–8], the contributions of Schegolev et al. [9–11] were the most influential in the field of organic conductors, where the technique was soon adopted widely [12–14] and by now is well known as the Schegolev method.

Laboratories all over the world (e.g. Chernogolovka, Göttingen, Los Angeles, Sherbrooke) utilize this technique on a regular basis; however, due to the elaborate analysis required and the discouraging costs of a single frequency point, the microwave cavity perturbation technique never became a standard method. Nevertheless, in the frequency range from 3 GHz to 300 GHz no other method can reach the sensitivity of enclosed cavities. By reviewing various applications on organic materials we want to show the advantages and versatility of the Schegolev method.

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2. Contactless Transport Measurements

If an enclosed resonator is slightly disturbed by introduction of a small object, the electrodynamic properties of this object can be evaluated from the perturbation if the geometry of the sample is known [15–17]. The change in the resonator properties are expressed by a complex quantity \( \hat{\omega} = \omega - i\Gamma/2 \)

\[
\frac{\Delta \omega}{\omega_0} = \frac{\Delta \omega}{\omega_0} = -\frac{i}{2} \frac{\Delta \Gamma}{\omega_0} = \frac{\omega_S - \omega_0}{\omega_0} - \frac{i}{2} \left( \frac{1}{Q_0} \right),
\]

where S and 0 indicate the filled and the empty cavity. \( \Delta \Gamma = \Gamma_S - \Gamma_0 \) is the change of the half width which is connected to the quality factor by \( Q = \omega_0/\Gamma \). \( \Delta \omega = \omega_S - \omega_0 \) is the change of the center frequency.

In the quasi-static regime (\( \hat{q}a \ll 1 \), where \( \hat{q} \) is the wavevector and \( a \) is the sample size, i.e. the sample is homogeneously penetrated by the electromagnetic field), the complex frequency shift \( \Delta \omega/\omega_0 \) is related to the complex dielectric constant \( \hat{\epsilon} = \epsilon' + i\epsilon'' \) by

\[
\hat{\epsilon} = 1 - \frac{\Delta \omega}{\omega_0} = \frac{\Delta \omega}{\omega_0} \left( \frac{1}{\gamma} + N \frac{\Delta \omega}{\omega_0} \right) + N^2 \left( \frac{\Delta \Gamma}{2\omega_0} \right)^2, \tag{2}
\]

as pointed out by Buravov and Schegolev for the first time [10]. In equation (2), \( N \) is the depolarization factor which can be calculated assuming an ellipsoid-shaped sample and \( \gamma \) is the resonator constant which depends on the volume of the sample and the cavity and the resonator mode excited.

In Figure 1 a typical setup is shown similar to the design used by Buravov and Schegolev [10]. The waveguide couples to the cylindrical copper cavity; a Teflon disk ensures that only the TE_{011} is excited. The sample is placed in one groove of a Teflon holder which is mounted on a quartz rod. By rotating the rod the specimen can be moved in and out of the cavity in order to measure the resonance parameters with and without the sample. The cavity is placed in the He exchange gas of a cryostat and can be heated for temperature dependent measurements. The common cavity designs are reviewed in [17]; a detailed discussion of the measurement technique can be found in [18–20].

From a technical point of view, the main advantage of high frequency measurements is that no contacts have to be attached, which in particular is a problem for tiny and fragile organic crystals. Thus no additional stress is applied which often causes microcracks or even the crystal to break upon cooling. Air sensitive samples may be sealed in quartz tubes or coated by grease and epoxy, for instance, and still measured in microwave cavities. Powder can be investigated, too, even without pressing it; just the volume fraction has to be known to get an absolute value [1,2,21].

3. Anisotropic Materials

For high frequency as well as for dc measurements, the anisotropy of big crystals can easily determined, by cutting specimen in various directions [22–24]. In the case of thin needle-like
Fig. 1. — Side view of a cylindrical cavity used for measurements at 7 to 12 GHz. The sample is placed in either of the grooves on the Teflon tray and in this configuration it will pass through the maximum electric field inside the cavity.

Fig. 2. — (a) Comparison between longitudinal (X, Z, Y) and transversal (Δ, +, 0) conductivity of (2,5-DCH₃-DCNQI)₂Cu. The measurements were done in cavities resonating at 10 GHz where the sample is placed in the antinode of the electric and of the magnetic field, respectively. Panel (b) shows the anisotropy factor $\sigma_\parallel / \sigma_\perp$ as a function of temperature.
crystals it is often not possible to arrange the contacts in the way necessary for the Montgomery-von der Pauw method commonly used to determine the dc-anisotropy. If no crystals with a large extension in the perpendicular direction are available, microwave measurements of the transverse conductivity in the maximum of the electric field are possible by placing a large number of samples side by side (e.g. [25]). Positioning the sample in the antinode of the magnetic field of a cavity (\( \mathbf{B} \parallel \) needle axis), eddy currents are induced in the plane perpendicular to the axis and allow to determine \( \sigma_\perp \). In Figure 2 the conductivity of \((2,5\text{-DCH}_3\text{-DCNQI})_2\text{Cu}\) in both orientations is plotted as a function of temperature as obtained by cavity measurements at 10 GHz [25]. The anisotropy significantly increases as the temperature is reduced mainly due to the temperature dependence of the longitudinal conductivity; the ratio is agreement with estimations of the overlap integral by NMR measurements [26]. Since the crystals grow as thin fibers with a typical diameter of 5 \( \mu \)m, the dc resistivity cannot be measured in the perpendicular direction; thus the microwave measurements for the first time show that the material is metallic even perpendicular to the chains.

The microwave technique gives the possibility to actually scan the conductivity of one sample by rotating it with respect to the electric field \( \mathbf{E} \). This can be done either by placing a disk-like sample in the axis of a circular cavity resonating in the \( \text{TE}_{010} \) mode [27]. If the sample is big enough and has low losses, the entire cross-section of the cavity can be covered; placing the thin sample in the center of a rectangular \( \text{TE}_{10p} \) cavity which is split in two parts as shown in Figure 3a, the angular dependence can be easily determined by rotation [27, 28]. Figure 3b demonstrates that a film of phthalocyanine can be grown well oriented with an anisotropy ratio \( \sigma_\parallel/\sigma_\perp \approx 10 \) [29]. With a similar method the angular dependence of reticulate doped polymers was determined [28], where \( \text{TTT}-(\text{TCNQ})_2 \) crystals grown anisotropically in a polyethylene
Fig. 4. — (a) Normalized temperature dependent microwave conductivity \( \sigma(T)/\sigma(300 \text{ K}) \) of \( \alpha-(\text{BEDT-TTF})_2\text{I}_3 \) in \( \mathbf{E} \parallel a \) and \( \mathbf{E} \parallel b \) direction. The dielectric constant \( \epsilon'(T) \) is displayed in the inset for both orientations. (b) Frequency dependent conductivity at \( T = 60 \text{ K} \) and \( T = 300 \text{ K} \). The symbols are obtained by different microwave cavities, the solid lines are from optical reflection measurements. The inset enhances the single particle gap at 400 cm\(^{-1}\) and a vibrational mode at 35 cm\(^{-1}\).
foil during casting. Depending on the preparation conditions, systems with an anisotropy ranging from 10 to $10^6$ can be obtained which is basically independent of temperature and frequency [27]. Since polarization microscopy shows that there are large homogeneous areas, the anisotropy is intrinsic to the crystals.

4. Study of Phase Transitions

Due to the reduced dimensionality, organic conductors commonly undergo phase transitions which significantly change their electronic properties. Similar to the dc transport, the high frequency measurements may show a sharp drop in conductivity, but often an interesting frequency dependence is observed in the insulating state. In Figure 4a the temperature dependent conductivity of the two-dimensional organic conductor $\alpha$-(BEDT-TTF)$_2$I$_3$ is displayed; the measurement was conducted at 10 GHz in both orientation, $E \parallel a$ and $E \parallel b$ [30]. While the dc conductivity rapidly drops below the metal-insulator transition $T_{MI} = 135$ K, the high-frequency data show a plateau of constant conductivity between 30 and 110 K which is strongly frequency dependent as displayed in Figure 4b. This phenomenon is not well understood yet [31]; hopping conducting and a Spin-Peierls ground state are discussed among others.
Fig. 6. — (a) Microwave conductivity of \( \alpha-(BEDT-TTF)_2I_3 \) for increasing doping concentration versus temperature along \( \mathbf{E} \parallel \mathbf{a} \) at 10.3 GHz. Duration of exposure to iodine (+) 60 min, (\( \bigtriangleup \)) 90 min, (\( \bigcirc \)) 120 min, (\( \bigtriangledown \)) 180 min, (\( \bigodot \)) 360 min. (b) Microwave conductivity of \( \alpha-(BEDT-TTF)_2I_3 \) at 60 K and 300 K for both crystal directions (\( \bigtriangleup \) for \( \mathbf{E} \parallel \mathbf{a} \), \( \times \) for \( \mathbf{E} \perp \mathbf{a} \)) as a function of duration of exposure to iodine.

From pressure studies it is known that DCNQI copper salts are in the vicinity of an insulating phase. Even the substitution of hydrogen by deuterium can dramatically change the temperature dependence of the conductivity (Fig. 2a) [32]. As seen in Figure 5, the conductivity of the deuterated derivatives \( (2,5-\text{DCD}_3-\text{DCNQI})_2\text{Cu} (d_8) \) and \( (3-\text{D},6-\text{D},2,5-\text{DCD}_3-\text{DCNQI})_2\text{Cu} (d_9) \) drops almost seven orders of magnitude, while \( (2,5-\text{DCH}_3-\text{DCNQI})_2\text{Cu} (h_8) \) remains outside the insulating phase at any temperature [25,33,34]. Most astonishing is the reentrant behavior if only 30% are substituted by \( d_8 \) [33]. In the low-conductivity region the microwave values are higher compared to the dc data (sometimes several orders of magnitude) indicating the existence of highly conducting areas even in the low conducting region. As their volume fraction undergoes the percolation threshold, they cannot be detected by dc measurements but probed by the high frequency technique.

5. Effects of Special Treatment

Since no contacts have to be attached and the same sample can be measured several times, microwave methods are frequently used to study the change in dielectric and transport properties of organic crystals upon irradiation [35], doping [36,37], polymerization [38] or thermal treatment [21]. In Figure 6a the change of the temperature dependence of the 10 GHz conductivity of a single \( \alpha-(BEDT-TTF)_2I_3 \) crystal is shown; after doping by iodine for more than one hour the low temperature conductivity starts increasing slightly without becoming superconducting (Fig. 6b) [37]. If \( \alpha-(BEDT-TTF)_2I_3 \) is tempered at 70°C it transforms to the superconducting
Fig. 7. — Microwave conductivity of a pressed sample of \( \alpha \)-(BEDT-TTF)\(_2\)I\(_3\) after stepwise annealing at 70 °C. Parameters added up annealing duration and volume fraction \( x \) of the \( \alpha_1 \)-phase. \( x \) is determined by fitting the curves from \( \sigma_p \) and \( \sigma_{pt} \) using \( \sigma(T) = (1 - x)\sigma_p(T) + x\sigma_{pt}(T) \).

\( \alpha_1 \)-phase (\( T_c \approx 8 \) K). Microwaves enable the measurement of the conductivity for stepwise annealing after every annealing step in always the same sample (Fig. 7) [21]. Similar experiments have been conducted on polymer films doped with \( \alpha \)-(BEDT-TTF)\(_2\)I\(_3\) [39]. In both cases the system can be described by a mixture of two components with changing ratio as the thermal treatment proceeds.

In Figure 8 the real and imaginary parts of the dielectric constant of disubstituted diacetylene DNP single crystals are shown as a function of temperature for different states of the solid state polymerization. The ferroelectric phase transition at \( T_c = 46.5 \) K shifts with advanced polymerization to lower temperatures and gets weaker [38]. The peak in the dielectric constant \( \varepsilon'(T) \) is getting flat. The dielectric losses \( \varepsilon''(T) \) first increase but after three hours of thermal treatment at 130 °C the peak decreases and finally no losses are found for full polymerization. This behavior indicates a lattice softening in the boundary between the polymerized part and the remaining monomer.
Fig. 8. — Temperature dependence of the real (a) and imaginary (b) part of the dielectric constant $\varepsilon = \varepsilon' + i\varepsilon''$ of a single DNP crystal measured at 10 GHz with the electric field parallel to the $b$-direction of the monomer. The variation with duration of thermal polymerization at 130 °C is shown for different periods of time as indicated.

6. Thermal Expansion

Besides the electrical transport, measurements of the resonance frequency allows for determination of the thermal expansion if needle shaped samples with high conductivity are placed in the electric field maximum of the enclosed resonator [40]. Figure 9 shows the relative thermal expansion of TTF-TCNQ; the Debye temperature is obtained from the fit of the data [41].

7. Frequency Dependence

In the first review by Schegolev [11] the most interesting point of the data on TCNQ complexes was the significant deviation of the high frequency data from the dc results at low temperatures and the large dielectric constant. While most examples mentioned above just utilize the contactless way of measuring the conductivity, the frequency dependence can give insight in the relevant transport mechanism. For a simple Drude-like metallic conduction, no frequency dependence is expected up to the far infrared spectral range, however, hopping conduction or collective transport like charge or spin density waves lead to a distinct frequency dependence even in the microwave range [42,43]. Since enclosed resonators are usually restricted to a single resonance frequency, either a large number of cavities have to be employed [18,44] or a special
cavity design with higher modes is used [45,46]. The frequency dependence of the conductivity of α-(BEDT-TTF)$_2$I$_3$ is displayed in Figure 4b; each of the data points at 2.3, 7, 10, 12, 24, 35, 60, and 100 GHz are taken in a different cavity setup. While at room temperature there is no significant frequency dependence, the low-temperature conductivity increases with frequency as $\sigma \propto \omega^s$ with $s = 1.3$ [31].

In Figure 10 the real and imaginary part of the room temperature dielectric constant of (TMTTF)$_2$BF$_4$ are shown as a function of frequency. The measurements are performed in long rectangular cavities as shown in Figure 3a which are excited in the TE$_{10p}$-mode with large $p$ of the order of 40 [46]. The increase in $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ together with the large value $\varepsilon' \approx 600$ indicates a strong mode at higher frequencies. The temperature dependence of the dielectric properties is displayed in the insets; at $T_{SP} = 40$ K (TMTTF)$_2$BF$_4$ undergoes a Spin-Peierls transition.

8. Summary

The Schegolev method is a well established technique to contactless measure small samples by placing them in a microwave cavity. The main applications on organic crystals are the determination of the temperature, frequency, and angular dependence of the conductivity, as
Fig. 10. — Real part $\epsilon'$ (left axis) and imaginary part $\epsilon''$ (right axis) of the dielectric constant of (TMTTF)$_2$BF$_4$ as a function of frequency at $T = 300$ K. $\sigma_1 \approx 0.23$ (Ωcm)$^{-1}$ and $\epsilon' \approx 600$. The insets show the temperature dependence of the conductivity $\sigma_1$ and the dielectric constant $\epsilon'$ measured at 9 GHz (open squares) and 23 GHz (solid squares).

well as the change upon irradiation, doping, or thermal treatment. Recently the microwave technique has been used to study the complex conductivity and penetration depth of organic superconductors like (BEDT-TTF)$_2$Cu(NCS)$_2$ in order to obtain information on the nature of the superconducting state [47]. The applications of this unique method are by far not exhausted yet.

References


