

Non-linear conductivity in morpholinium (TCNQ)₂ salts

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Received 27 August 1986

Abstract. We report measurements of non-linear current–voltage characteristics and harmonic distortions in the conductance of several morpholinium (TCNQ)₂ salts. The harmonic distortions show that there is no threshold field for the onset of non-linearities in the conductivity. Furthermore they show that the I – V characteristics can be expanded in Taylor series around $E = 0$. A simple expression is proposed to describe the non-linearities at low fields. At high fields the relative change in conductivity is approximately the same for most materials investigated. This suggests that the transport mechanisms at high fields and at low fields are related.

1. Introduction

Non-linear conductivity has been observed in a number of quasi-one-dimensional conductors. It has been studied extensively in trichalcogenides like NbSe₃ (see e.g. Ong and Monceau 1977, Grüner 1983, Monceau 1982) and the idea has generally been accepted that the non-linear conductivity in these materials is caused by the depinning of incommensurate charge-density waves (CDWs). Models that describe the pinning of the CDWs by random impurities lead to relations that are used to describe the conductivity σ as a function of electric field strength E . The equations used by Grüner (1983) are:

$$\begin{aligned}\sigma(E) &= \sigma_1 \quad E \leq E_T \\ \sigma(E) &= \sigma_1 + \sigma_2 (1 - E_T/E) \exp[-E_0/(E - E_T)] \quad E > E_T.\end{aligned}\tag{1}$$

In equation (1) E_T is the threshold field for the depinning of CDWs. Evidence for the existence of such a threshold was first presented by Fleming and Grimes (1979). For a recent review on the subject of CDW transport see the paper of Gill (1986).

In a number of charge-transfer salts conductivity seems to be perfectly linear at low fields but at higher fields non-linear conductivity has been observed too. Examples are quinolinium (TCNQ)₂ (Mihály *et al* 1979) and (MeEtM)_{1-x}(MeEtthio-M)_x (TCNQ)₂ (Kramer *et al* 1985). In these materials the non-linear current–voltage (I – V) characteristics exhibit no observable threshold field and can be adequately described by an equation used by Ong and Monceau (1977) and Kramer *et al* (1985)

$$\sigma(E) = \sigma_1 + \sigma_2 \exp(-|E_0/E|^\alpha)\tag{2}$$

where α is an adjustable parameter. Note that equation (1) differs from equation (2)

mainly by the presence of the threshold field E_T in (1). Recently, evidence for the existence of a threshold field in the non-linear conductivity of TTF-TCNQ has been reported by Laco *et al* (1985). This is in agreement with the observations in trichalcogenides because TTF-TCNQ is also a system with incommensurable CDWs.

The question arises whether the mechanisms that cause the non-linear conductivities in trichalcogenides and in charge-transfer salts with commensurable CDWs are similar. There is evidence that the mechanism in trichalcogenides is different from the one in charge-transfer salts with commensurable CDWs. Above the threshold field the noise power spectra of trichalcogenides exhibit sharp peaks at frequencies that depend on the electric field (Gill 1986). These peaks are usually attributed to the same depinning of incommensurable CDWs that is considered responsible for the non-linear conductivities in these materials. Depinning of commensurable CDWs is unlikely to occur and, indeed, noise power spectra of charge-transfer salts with commensurable CDWs (Jos and Zijlstra 1986, Jos *et al* 1987a, b) do not show any peaks. It would be interesting to know whether there is a threshold field in the conductivity of these charge-transfer salts. In other words, is the linear conductivity observed at low fields as perfectly linear as it seems? As stated before it is difficult to discover a threshold field in I - V characteristics. Measurements of the generation of third and higher harmonics are more likely to reveal a possible threshold field. This technique has been applied to TaS₃ by Miller *et al* (1985).

In this paper we report measurements of the I - V characteristics of and harmonic distortion in several members of the morpholinium (TCNQ)₂ family. These compounds are charge-transfer salts with commensurable CDWs. The materials are denoted by R₁R₂ thio-morpholinium (TCNQ)₂, where R₁ and R₂ are the substituents on the morpholinium molecules. The symbols used for R₁ and R₂ are: H for hydrogen, Me for methyl, Et for ethyl and Bu for n-butyl. We shall abbreviate thio-morpholinium to thio-M. In this way for example methyl-ethyl-morpholinium (TCNQ)₂ is abbreviated to MeEtM(TCNQ)₂.

2. Experimental set-up

Ohmic contacts were made on the crystals with gold filaments glued to the crystal ends with silver paint (Leitsilber 200). The crystals were placed in a nitrogen gas atmosphere to prevent drift of the conductivity due to aging which can occur when samples are in contact with the air after application of the contacts.

The experimental set-up for measuring the I - V characteristics at high field strengths is shown in figure 1. All measurements were performed at room temperature except those on uniform MeEtM(TCNQ)₂ which were done at $T = 340$ K. In order to minimise Joule heating effects, voltage pulses of short duration $t_p \approx 6 \times 10^{-6}$ s were applied at intervals $t_r \approx 9.4 \times 10^{-3}$ s. The voltage pulses were observed with an oscilloscope and the amplitude was measured with the help of a sample-and-hold unit (SHU1) that was triggered by a delayed trigger pulse of the oscilloscope. This enabled us to measure the amplitude at any desired time during the pulse. In figure 1 the crystal is denoted by R_s. The current pulse was measured with the help of another sample-and-hold unit (SHU2) and a 10 Ω metal film resistor. The impedances of the samples were always much larger than 10 Ω. In this way a possible drift of the current during the voltage pulse could be detected. We checked on Joule heating effects by increasing the pulse duration and verifying whether the amplitude of the current pulse remained unaltered. With this method we could apply electric field strengths of up to 5000 V m⁻¹ to most of the materials investigated without causing Joule heating effects.

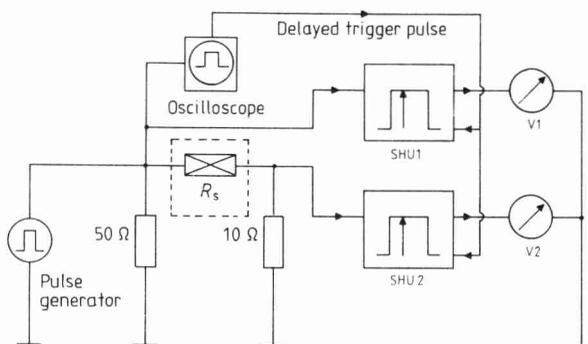


Figure 1. The experimental set-up for the pulsed measurements of the I - V characteristics. The broken lines around the sample (R_s) denote the container with a nitrogen gas atmosphere. V_1 and V_2 are voltmeters.

In figure 2 the experimental set-up for the measurements of third and higher harmonics is shown. A sine wave with a frequency of 1250 (or 625) Hz was generated and the higher harmonics of the generator were suppressed by the filter with a band width of $\frac{1}{3}$ octave and an attenuation of more than 50 dB at 1 octave. The amplifier acted as an impedance match between the filter and the crystal (denoted by R_s in figure 2). The third and higher harmonic components in the current response to the applied sine wave were detected with the help of a 10 Ω resistor and a wave analyser. The component with the frequency of 1250 (or 625) Hz was suppressed by an adjustable bridged T filter (attenuation ≥ 40 dB) to prevent inter-modulation distortion and overload of the wave analyser. The analyser used was a Brüel and Kjaer 2033 Fast Fourier Transformer or a Hewlett Packard 358A Spectrum Analyser. The amplitude of the sine wave was always kept small enough to suppress Joule heating effects. In order to determine a harmonic-frequency component generated by the sample, three measurements were done: (i), A measurement of the harmonic-frequency component generated by the sample and the network together u_s ; (ii), A measurement of the component generated by the network u_r . During this measurement the sample was replaced by a metal film resistor with the same resistance; (iii), A measurement of the background noise voltage corrected for the effective band width of the analyser u_n . The amplitude of the harmonic-frequency component generated by the sample is

$$(u_s^2 - u_n^2)^{1/2} \pm (u_r^2 - u_n^2)^{1/2}.$$

The sign depends on whether the phases of the components generated by the sample and by the network are equal or opposite. In our measurements the second term

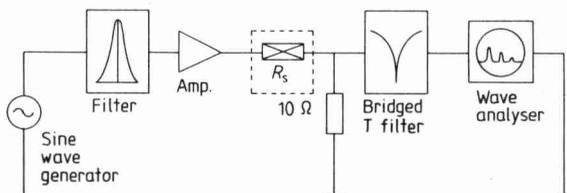


Figure 2. The experimental set-up for the measurements of the generated harmonic components in the current of the sample (R_s).

was always negligible compared to the first. As with the measurements of the I - V characteristics the samples were kept in a nitrogen gas atmosphere. All measurements were done at room temperature.

3. Results

As stated in the Introduction the I - V characteristics can be adequately described by equation (2). In figure 3 typical non-linear I - V characteristics of MeBum(TCNQ)₂ are shown. The broken curve is based on equation (2) with $\alpha = 0.52$. The full curve is discussed later. Figure 4 shows typical non-linear I - V characteristics of HButhio-M(TCNQ)₂. The broken and full curves will also be discussed later. The characteristics of all members of the morpholinium (TCNQ)₂ family investigated look similar. It appeared

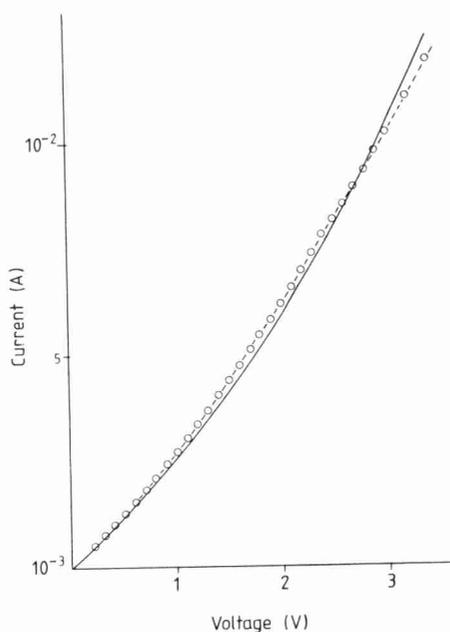


Figure 3. The I - V characteristics of an MeBum(TCNQ)₂ sample. The broken curve is a fit to equation (2*), the full curve to equation (4), see text.

that the conductivities could be also fitted to equation (2) if $\alpha = 1$. The results are somewhat poorer but this fitting procedure is a quick and simple way to compare the non-linearities of different samples. The non-linear conductivity were therefore all fitted to the equation

$$\sigma(E)/\sigma(0) = 1 + a \exp(-E_1/|E|). \quad (3)$$

The parameters a and E_1 are listed in table 1.

The main inaccuracy in the results arose from the offset of SHU2. This led to an

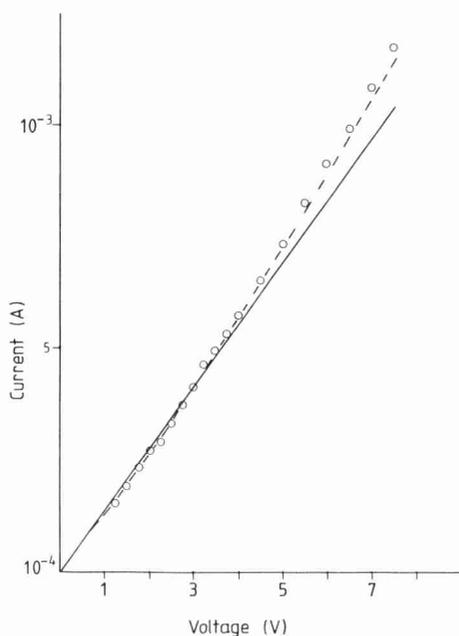


Figure 4. The I - V characteristics of an HButhiom(TCNQ)₂ sample. The meaning of the symbols are as in figure 3.

absolute resolution in the measured current-pulse amplitude of $40 \mu\text{A}$. This inaccuracy has been taken into account in the fitting procedures, the relative qualities of which are shown by the values for χ^2 . Note that $a \approx 1$ except for dimerised MeEtM(TCNQ)₂ and $E_1 \approx 1\text{--}2 \text{ V mm}^{-1}$ except for dimerised MeEtM(TCNQ)₂ and HButhio-M(TCNQ)₂. The better the conductivity the larger a seems to be.

We checked our experimental procedure with a commercially available solid state diode. We measured the I - V characteristics and fitted them to the equation

$$I = I_0 (e^{V/V_0} - 1)$$

where I_0 and V_0 are the fitting parameters. With the use of this equation and the values

Table 1. The fitting results of the I - V characteristics to equation (3).

Compound	$\sigma(0) (\Omega \text{ cm})^{-1}$	a	$E_1 (\text{V mm}^{-1})$	χ^2	Remarks
HEtM(TCNQ) ₂	3.2×10^{-2}	0.59 ± 0.07	4.3 ± 1.0	1.8	$T = 300 \text{ K}$
MeBuM(TCNQ) ₂	~ 5	1.27 ± 0.17	0.59 ± 0.04	4.5	300 K
MeEtthiom(TCNQ) ₂	2.7	1.01 ± 0.11	1.7 ± 0.4	4.8	300 K
MeEtM(TCNQ) ₂	30	2.5 ± 0.7	0.49 ± 0.05	1.8	300 K ^a
MeEtM(TCNQ) ₂	1.5×10^{-3}	0.19 ± 0.04	13 ± 2	0.2	300 K ^b
HBuM(TCNQ) ₂	0.43	1.0 ± 0.2	1.3 ± 0.4	20	300 K
HButhiom(TCNQ) ₂	0.19	0.53 ± 0.12	26 ± 8	4.7	300 K

^a Uniform phase.

^b Dimerised phase.

for I_0 and V_0 obtained by the fit, we calculated numerically the third harmonic component in the current response to an applied AC voltage. We measured the third harmonic component in the way described above and found that the calculated and measured values were equal within 10%.

The generation of harmonic components in the current response to an AC voltage was observed in all samples investigated: $\text{HEtM}(\text{TCNQ})_2$, $\text{HBuM}(\text{TCNQ})_2$, $\text{MeEtthioM}(\text{TCNQ})_2$, $\text{MeBuM}(\text{TCNQ})_2$ and $\text{HButhio-M}(\text{TCNQ})_2$. Only the latter two were examined extensively. In the other compounds we only observed that the amplitude of the i th harmonic component was proportional to the i th power of the AC voltage.

In figure 5 the generated third harmonic component I_3 in the current of the $\text{MeBuM}(\text{TCNQ})_2$ sample of figure 3 is shown as a function of applied effective AC voltage V_{AC} . Note that I_3 is proportional to V_{AC}^3 . In figure 6 several higher harmonics of the $\text{HButhio-M}(\text{TCNQ})_2$ sample of figure 4 are plotted versus applied voltage. The fifth and higher harmonics were difficult to observe at low applied AC voltages. However, the measurements are compatible with the assumption that at low voltages the i th harmonic component I_i is proportional to V_{AC}^i . The broken and full curves in the figures are discussed in the following section.

We also observed weak second harmonic components in all samples investigated. These components were proportional to V_{AC}^2 . The occurrence of even harmonic components suggests some rectifying action by the crystal or the metal-crystals interface. However, this effect was too small to be observed in the I - V characteristics. It is certainly negligible compared to other non-linear effects at all but the lowest voltages.

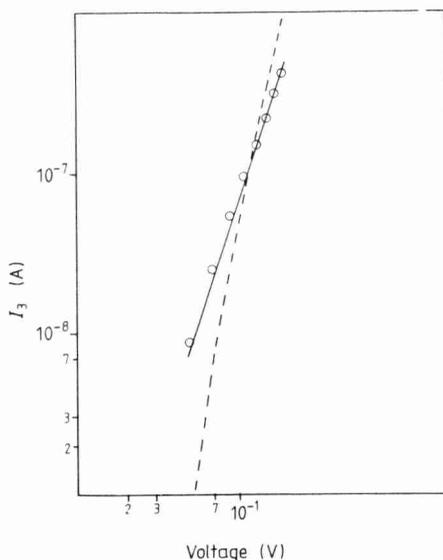


Figure 5. The third harmonic component I_3 in the current of an $\text{MeBuM}(\text{TCNQ})_2$ sample plotted against AC voltage. The meaning of the symbols are as in figure 3.

4. Discussion

The parameter a of equation (3) is ~ 1 for most compounds of table 1. The parameter $E_1 \approx 1\text{--}2 \text{ V mm}^{-1}$ for most compounds. Hence the relative change in the conductivity is

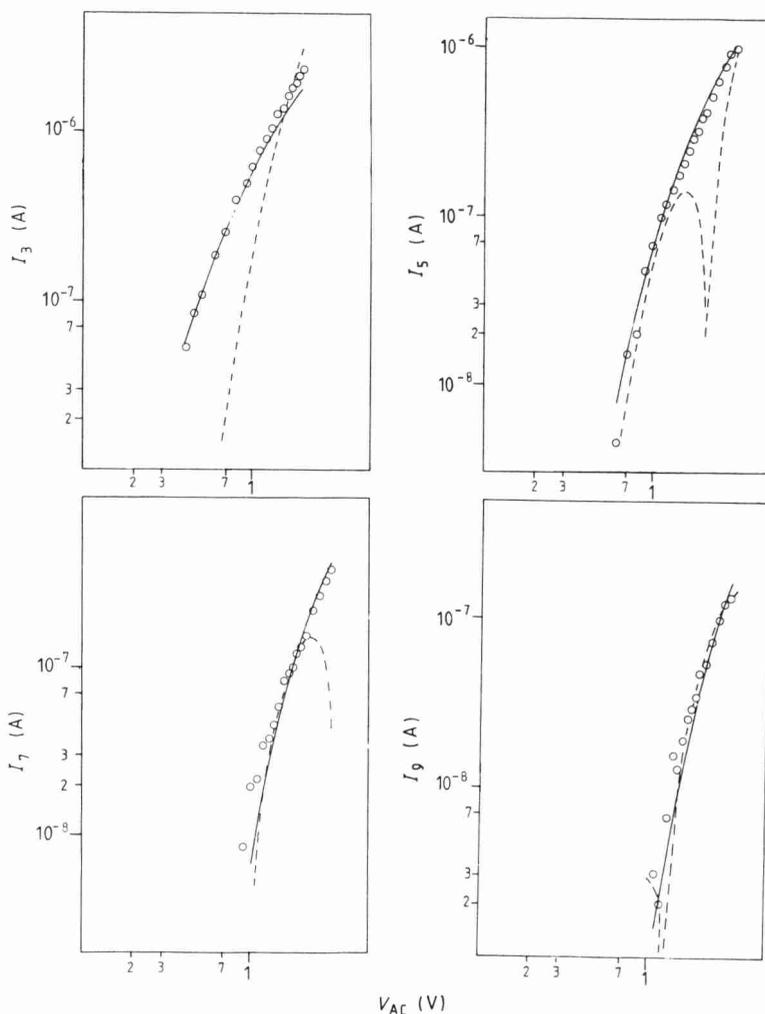


Figure 6. The harmonic components in the current of an HButhiom(TCNQ)₂ sample plotted against AC voltage. I_3 is the third harmonic component, I_5 the fifth, I_7 the seventh and I_9 the ninth harmonic component. The meaning of the symbols are as in figure 3.

approximately the same for all materials. This suggests that the conduction mechanism in the non-linear regime is related to the mechanism in the linear regime. This has been suggested before by Kramer *et al* (1985). The scaling of all I - V characteristics indicates that the conduction mechanisms of all compounds investigated are similar. We recall that analysis of noise measurements led to the same conclusion (Jos *et al* 1987a,b).

We have tried to obtain more information about the electric transport in the non-linear regime by measuring the current noise power spectrum. Experimental details are published elsewhere. Joule heating effects are strongly present when a DC current is applied in the non-linear regime and hence the crystal temperature is unknown. However, we could not eliminate Joule heating effects by performing pulsed measurements of the current noise as has been done by Westera (1982), because pulsed measurements would only yield information about the current noise spectrum at high

frequencies. The information that has been useful in revealing the electric transport mechanism in the 'ohmic' regime, was obtained in the 'low'-frequency range between 10 Hz and 10 MHz (Jos *et al* 1987a,b). Therefore we wanted to follow the same procedure in the non-ohmic regime. Many attempts to measure the noise spectrum in the non-ohmic regime failed due to crystal breakdown, probably as a result of Joule heating or high electric field strengths. Only a sample of HETm(TCNQ)₂ survived long enough for the measurement of current noise spectra at $I = 10^{-4}$ and 3×10^{-3} A. At both currents only $1/f$ noise could be observed. The magnitude of the $1/f$ noise at 3×10^{-3} A was 500 times larger than the magnitude at 10^{-4} A. No peaks or other details like lorentzians were observed in the frequency range between 10 Hz and 10 MHz. So far there is no theory to explain this $1/f$ noise. Hence we cannot deduce information about the nature of the non-linear charge transport from this observation of $1/f$ noise.

Harmonic components were observed in the current response to an AC voltage in the 'ohmic' part of the I - V characteristics. Harmonics occurred even at small voltages. No evidence for the existence of a threshold field could be found. So equation (1) is not a good description of the I - V characteristics in these materials. The magnitude of the i th harmonic components was proportional to V_{AC}^i at low voltages. This is evidence that the I - V characteristics can be expanded in Taylor series in V around $V = 0$. However, equation (2) cannot be expanded in such a Taylor series because all derivatives of the exponential term are zero at $E = 0$. So we conclude that equation (2) might be an adequate description of the I - V characteristics at high fields but at low fields it is incorrect.

An empirical equation that describes the I - V characteristics and that can be written as a Taylor series around $V = 0$ is a Padé approximant:

$$I = \frac{V}{R} \left(\frac{1 + b_1 E^2}{1 + b_2 E^2} \right). \quad (4)$$

Equation (4) has the same number of free parameters as equation (3). However, the I - V characteristics of MeBum(TCNQ)₂ samples were better described by equation (4). The values for χ^2 of fits to equation (4) were about half the values for χ^2 of fits to equation (3). In fact, the I - V characteristics could be described just as well by equation (4) as by equation (2), which has one extra free parameter. We fitted the I - V characteristic of the MeBum(TCNQ)₂ sample of figure 3 to equation (2), rewritten as

$$I = (V/R)[1 + c \exp(-|E_0/E|^\alpha)]. \quad (2^*)$$

The result is shown by the broken curve in figure 3. The parameters had the values: $c = 1.94$, $E_0 = 1.94 \text{ V mm}^{-1}$ and $\alpha = 0.52$. The predicted third harmonic component I_3 is given by the broken curve in figure 5. The predicted values do not agree with the observed values for I_3 .

We also fitted the I - V characteristics and the third harmonic component of the MeBum(TCNQ)₂ sample to equation (4). The results of this combined fit are shown by the full curves in figures 3 and 5. The values for b_1 and b_2 were $1.25 (\text{V mm}^{-1})^{-2}$ and $0.38 (\text{V mm}^{-1})^{-2}$, respectively. The third harmonic component is described very well (figure 5) but the observed I - V characteristics are less non-linear than the fit predicts.

We fitted the I - V characteristics and I_3 , I_5 , I_7 and I_9 of the HButhiom(TCNQ)₂ sample of figures 4 and 6 simultaneously to equation (4). The results are shown by the full curves in figures 4 and 6. The values for the parameters were $b_1 = 0.658 (\text{V mm}^{-1})^{-2}$ and $b_2 = 0.620 (\text{V mm}^{-1})^{-2}$. The harmonic components are described very well. This proves that

the Padé approximant (4) is a good description of I - V characteristics at low fields. The agreement between the combined fit and the observed I - V characteristics is poor. It was possible to fit the I - V characteristics and the higher harmonics simultaneously to equation (2*). The results are shown by the broken curves in figures 4 and 6. The agreement with the observed I - V characteristics is good but there is no agreement with the observed I - V characteristics is good but there is no agreement between equation (2*) and the observed harmonic components. The values of the parameters were: $c = 0.28$, $E_0 = 3.37 \text{ V mm}^{-1}$ and $\alpha = 1.1$

5. Conclusion

We find that the I - V characteristics of morpholinium (TCNQ)₂ salts can be expanded in Taylor series in V around $V = 0$. The Padé approximant (4) describes the I - V characteristics very well at low field strengths since it yields the right amplitudes of four higher harmonic components (I_3 , I_5 , I_7 and I_9) using only two parameters. This description fails, however, beyond this range of field strengths. Hence we conclude that there must be additional non-linearities not described by equation (4) that are also responsible for the I - V characteristics at high fields.

In normal semiconductors non-linear conductivity can arise from a field dependence of the mobility. However, in that case the conductivity usually decreases at high fields. In our compounds the conductivity increased. We have argued elsewhere (Jos *et al* 1987a) that the conductivity in morpholinium (TCNQ)₂ salts is determined by the detrapping rate of the charge carriers. It seems realistic to assume that at high electric field strengths the detrapping rate is enhanced. The observed non-linear conductivities are therefore compatible with the model for the electric transport derived earlier.

Acknowledgments

We thank Dr J de Boer of the Chemistry Department of the University of Groningen for supplying the crystals. This work was performed as part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO).

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