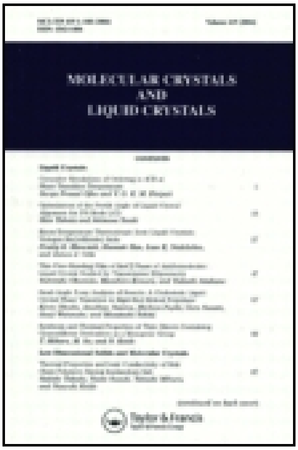

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SHOT NOISE IN THE ELECTRIC TRANSPORT IN SOME MORPHOLINIUM-TCNQ SALTS

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Abstract We report the occurrence of shot noise in ohmic conducting Morpholinium-TCNQ salts. The presence of shot noise indicates that the conduction mechanisms in these materials must be very different from those in normal semiconductors and metals.

The compounds studied are Methyl-Ethyl Morpholinium $(TCNQ)_2$ ($MEM(TCNQ)_2$) ,which has a dimerized, semiconducting phase below 335 K and a uniform, metallic phase above 335 K [1], and Methyl-Butyl Morpholinium-$(TCNQ)_2$ ($MBM(TCNQ)_2$) ,which has uniform stacks as well as dimerized stacks at room temperature [2].

Details about sample preparation and experimental procedures will be published elsewhere [3].

In the semiconducting phase of $MEM(TCNQ)_2$ we found the activation-energy of the conductivity to be 0.8 eV around 300 K and 0.35 eV between 313 K and 335 K, see also ref. 4. The noise measurements were done in the latter regime. Here the value of the conductivity $\sigma_{//}$ is typically 1 $(\Omega cm)^{-1}$ The noise measurements on $MBM(TCNQ)_2$ were performed in the temperature range from 250 K to 315 K. Typical values for $\sigma_{//}$ are 10 - 10^2 $(\Omega cm)^{-1}$ and 0.3 eV for the activation energy.

For both materials the current-voltage characteristics were ohmic at least at electric fields between 6.7 V/m and 2.10^4 V/m. The ac-impedances were frequency independent from 0 Hz up to 10^7 Hz.

In addition to the thermal noise we found an excess noise consisting of $1/f^\alpha$ noise, where $0.9 < \alpha < 1.1$,and a contribution which we have analyzed in terms of Lorentz spectra of the form $S_I(0)/(1+\omega^2\tau^2)$. A typical computer analysis of the excess noise in $MBM(TCNQ)_2$ is shown in figure 1. The noise has been decomposed into a $1/f^\alpha$ component and two Lorentzians. Computer analysis of the excess noise always showed one Lorentzian in spectra of $MEM(TCNQ)_2$ and two Lorentzians in spectra of $MBM(TCNQ)_2$. The low frequency noise levels of the Lorentzians are proportional to the current and independent of the crystal dimensions. Four probe measurements showed that the source of the Lorentzian noise lies in the crystal and not in the contacts. The temperature dependences of $S_I(0)/I$ and τ are plotted in figure 2 for $MBM(TCNQ)_2$ and in figure 3 for $MEM(TCNQ)_2$. The activation energies for $S_I(0)/I$ and τ are the same in $MEM(TCNQ)_2$ (0.55 eV) and also for the first Lorentzian in $MBM(TCNQ)_2$ (0.70 eV). In this material the second Lorentzian has a temperature independent low frequency level at $S_I(0)/I = 4 \pm 2\ 10^{-19}$ A.s averaged over several samples with various dimensions. The same level was found in the uniform phase of $MEM(TCNQ)_2$ at 353 K, suggesting that the temperature dependent Lorentzians are associated with dimerized stacks of TCNQ molecules and Lorentzians with temperature independent low frequency levels with uniform stacks.

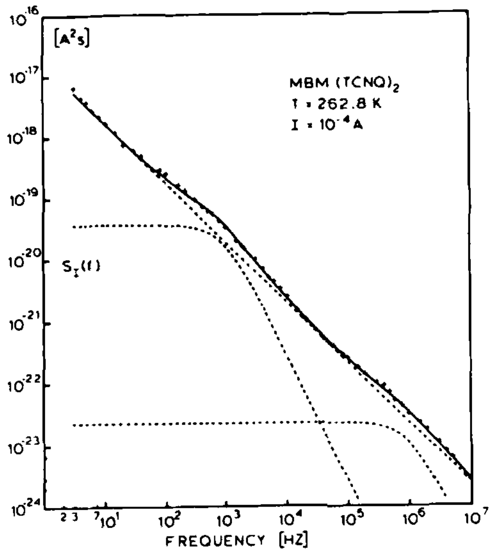

FIGURE 1 The noise in excess of thermal noise versus frequency. The dotted lines are the $1/f^{\alpha}$ component and the Lorentzians , the solid line is the sum of these components.

This simple picture is corroborated by the fact that in $MBM(TCNQ)_2$, which has uniform stacks as well as dimerized stacks, we always find two Lorentzians.

The amplitude of the $1/f^{\alpha}$ noise is always proportional to the square of the current, in contrast with the Lorentzian noise components where the low frequency noise levels are proportional to the current and $S_I(0)/I$ is independent of the crystal dimensions. This suggests an interpretation of the Lorentzian shaped noise components in terms of shot noise.

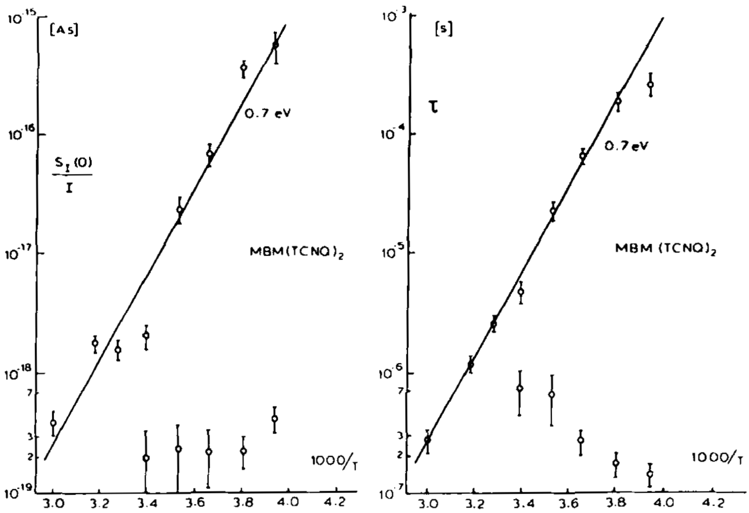

FIGURE 2 Relative low frequency levels and characteristic times versus temperature for $MBM(TCNQ)_2$.

When charges q are transported over a distance ℓ in a crystal with contact-spacing L in a finite time τ at an average rate λ, the average current is given by : $\bar{I} = \lambda q(\ell/L)$. If the current pulses are assumed to be rectangular and occurring at random,according to Carson's theorem [5], the current noise is given by :

$$S_I(f) = 2qI\ (\ell/L)\ \left(\frac{\sin \frac{1}{2}\omega\tau}{\frac{1}{2}\omega\tau} \right)^2$$

Note that λ should be proportional to the electric field to obey Ohm's law. With an appropriate distribution of the duration times around an average value τ_o this reduces to something with the shape of a Lorentzian with a characteristic time τ_o , though slight deviations of the Lorentzian shape can not be detected experimentally because of the large $1/f^\alpha$ noise.
The relative low frequency noise level is: $S_I(0)/I = 2q\ \ell/L$.

It should be stressed that the occurrence of shot noise in ohmic conductors is highly unusual. In fact we know of no other example.

We found for uniform stacks $S_I(0)/I = 4\ 10^{-19}$ A.s. This level is found to be independent of L, hence ℓ must be proportional to L. The simplest assumption is ℓ=L in which case we find $q \simeq e$, where e is the electron charge. The noise measurements therefore suggest that the current flows in pulses occuring at random in which one electron charge is transported through the crystal in a time τ_o without being scattered or trapped. Note that in MBM(TCNQ)$_2$ almost all current must go through the uniform stacks in order to obtain the same low frequency level as in the uniform phase in MEM(TCNQ)$_2$. We found the time τ_o and hence the velocity of the electron charge to be independent of the electric field. A possible explanation could be the presence of solitons or CDW's moving in the uniform stack [6] at a rate λ proportional to the electric field, each carrying one electron charge. In dimerized TCNQ stacks we found $S_I(0)/I$ to be much larger than two electron charges at low temperatures. This can be explained by assuming that the moving solitons or CDW's transport more than one electron charge through the crystal, for instance we can write $q\ell/L = e\tau_o/\tau_t$ where τ_t is the transit time of the soliton or CDW. In this case τ_o is larger than τ_t. This also would explain the occurrence of the same activation energies in $S_I(0)/I$ and τ_o. Here we also found the time τ_o to be independent of the electric field.

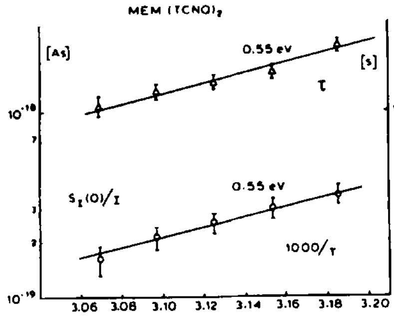

FIGURE 3 Relative low frequency levels and characteristic times versus temperature for MEM(TCNQ)$_2$.

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