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# 1/*f* noise in conducting Langmuir-Blodgett films

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Measurements of spectral characteristics of electric noise in conducting Langmuir-Blodgett (LB) films of $(C_{16}H_{33}\text{-TCNQ})_{0.4}(C_{17}H_{35}\text{-DMTTF})_{0.6}$ prepared by the vertical lifting technique have been carried out. $[(C_{16}H_{33}\text{-TCNQ})_{0.4}(C_{17}H_{35}\text{-DMTTF})_{0.6}$ denotes the surface-active charge-transfer complex of hexadecyltetracyanoquinodimethane ($C_{16}H_{33}$-TCNQ) and heptadecyldimethyltetrathiofulvalene ($C_{17}H_{35}$-DMTTF).] Excess $1/f$ noise has been observed over the frequency range of $1-10^4$ Hz. We found that the noise power is proportional to the square of dc current flowing through the sample and has a power spectrum varying approximately as $f^{-1}$ over the frequency range studied. The noise power is three orders of magnitude larger than that predicted by Hooge's formula. A theoretical model for the origin of $1/f$ noise due to fluctuations of the number of charge propagation paths in the sample is proposed. The calculations of $1/f$ noise level using this model are in quantitative agreement with experimental results not only in the LB films but also in tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) crystals. [S0163-1829(98)02920-8]

## I. INTRODUCTION

The Langmuir-Blodgett technique is now intensively studied since it gives the possibility of organizing electron donor and acceptor molecules at the molecular level. The aim is to produce charge-transfer complexes in the form of ultrathin films suitable for utilization in molecular-scale devices. The LB films of surface-active derivatives of charge-transfer complexes of TTF and TCNQ are very promising for using in molecular electronic (ME) devices because of their homogeneity and stability.[1,2] Unfortunately, the weak point of these films is their comparatively low conductivity (0.1–1 S/cm usually). These values lie far below (about three orders of magnitude) the conductivity values of the corresponding bulk TTF-TCNQ crystals. It reduces significantly the area of possible applications of these films in ME. The fact that the electrical transport mechanism of the films is insufficiently studied hinders progress in preparation of films with higher conductivity. Due to the low dimensionality of the LB films this mechanism could have several features that are not observed in bulk TTF-TCNQ crystals. In this context it is clear that the study of conduction mechanisms not only can allow one to increase the film conductivity but also can lead to new physical phenomena.

Noise measurements are shown to be an effective technique for studying electrical transport mechanisms since data on the number of charge carriers and their lifetime can be obtained. It is well known that noise imposes a practical limit on the performance of the electronic devices. Therefore, a knowledge of LB film noise characteristics allows one to appreciate prospects for their applications in ME devices.

In this paper the measurements of electrical noise in conducting LB films are presented for the first time. Excess $1/f$ noise has been observed over the frequency range of $1-10^4$ Hz. We also suggest a theoretical model for the origin of $1/f$ noise. The calculations of the $1/f$ noise level using this model are in quantitative agreement with experimental results not only in the LB films but also in TTF-TCNQ crystals.

## II. SAMPLE PREPARATION

The samples were prepared using the LB technique. Explicit description of this technique is contained in Ref. 3, where further details can be found. The monomolecular layer was formed by mixing benzene solutions ($7\times10^{-4}$ mole/l concentration) of $C_{16}H_{33}$-TCNQ and $C_{17}H_{35}$-DMTTF (Fig. 1) in a 1:1.5 molar ratio and spreading the mixture onto a ultrapure water surface in a KSV-5000 trough. The monolayer was transferred at a constant surface pressure of 20 mN/m by the vertical lifting technique onto the stringently cleaned sapphire substrate with prefabricated chromium electrodes. The area per molecule $A$ in the process of deposition

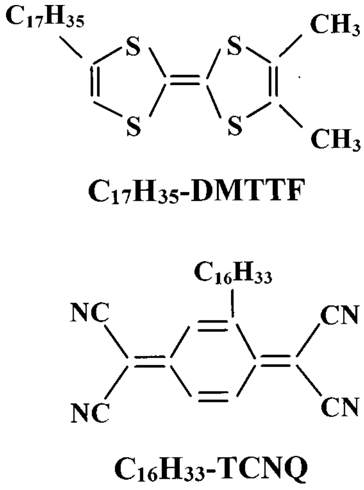

FIG. 1. Materials used in this study.

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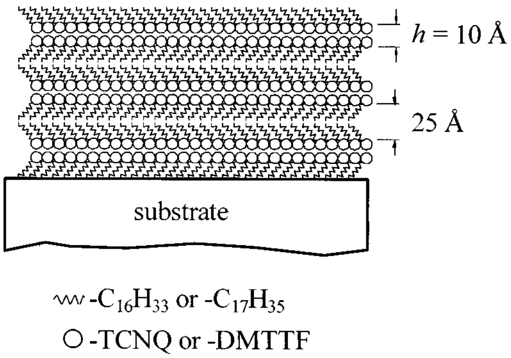

FIG. 2. Schematic representation of the cross section of $Y$-type LB film consisting of six monolayers.

was about of 20 Å$^2$. Dipping speed was 5 mm/min for the upstroke deposition mode and 3 mm/min for the downstroke one. All the prepared samples were of $Y$ type (see Fig. 2). After LB film deposition the samples were transferred to a vacuum chamber where they were stored under vacuum for at least a week to remove residual water before the measurements (our experience had shown that this process led to obtaining reproducible noise spectra).

In this paper we present results of noise measurements of four samples whose resistances ranged from 160 Ω (sample 3) to 1 MΩ (sample 1). All samples had linear voltage-current characteristics in the current range of $10^{-8}-10^{-5}$ A. The film characteristics and geometrical parameters of electric contacts of the samples are summarized in Table I. The room-temperature lateral (in-plane) conductivity $\sigma$ have been calculated by assuming that LB films consist of alternating conducting layers (see Fig. 2) with thickness $h = 10$ Å (formed by -TCNQ and -DMTTF head groups) along which charge propagation occurs, and nonconducting layers with thickness 25 Å (formed by $-C_{16}H_{33}$ and $-C_{17}H_{35}$ side groups). Therefore, $\sigma = 2d/(R_{\mathrm{sample}} h w N_l)$, where $R_{\mathrm{sample}}$ is the sample resistance, $d$ and $w$ are the distance between the electrodes and the width of the ones, respectively (see Fig. 3), and $N_l$ is the number of layers.

### III. EXPERIMENTS AND RESULTS

The noise measuring setup is shown schematically in Fig. 4(a). Due to the high resistances of the samples studied, the noise was measured by applying a constant voltage to the sample and recording the current fluctuations. We used two-probe configuration for noise measurements since high resistances of the samples and stray capacitances prohibit the use of both five-probe ac and four-probe dc techniques. To prevent ac pickup and interference from other sources of electromagnetic fields, all units of the setup were electrically screened and the voltage supply was provided by dry batteries. Since the high level of intrinsic low-frequency noise is inherent in the dry batteries themselves the current was supplied to the sample through the first-order low-pass filter with a cutoff frequency of $10^{-2}$ Hz. We used a quiet metal-film resistor as a calibrated one $R_{\mathrm{calib}}$ and a low-noise preamplifier with a field effect transistor input stage.

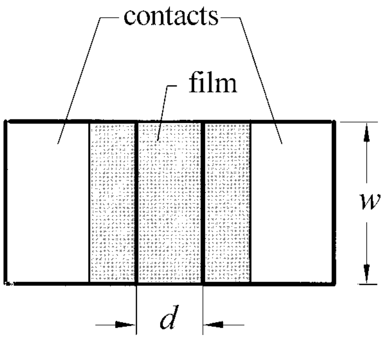

FIG. 3. Sample and electrode geometry.

As shown in Fig. 4(a), voltage fluctuations on the calibrated resistor were amplified by a preamplifier and by a selective amplifier with variable band-pass filter. Being a part of the selective amplifier the band-pass filter played the role of an antialiasing filter restricting the frequency range of original data prior to analog-to-digital conversion. Estimations of noise spectral density were performed using Fourier transformation of the measured signal. We followed recommendations from Ref. 4 in our calculations. Spectral densities were estimated by averaging 200 squared absolute values of Fourier transforms of subrecords (noise realizations), so the normalized error was $\varepsilon = 1/\sqrt{200} \approx 0.07$. Two types of subrecords were registered: one for spectral density estimations in the frequency range of $1-10^4$ Hz with a resolution of 21 Hz, and another for spectral density estimations in the frequency range of 1–150 Hz with a resolution of 0.65 Hz.

TABLE I. Parameters of the samples. $N_l$ is the number of layers, $d$ and $w$ are the distances between the electrodes and their widths, respectively (see Fig. 3), and $\sigma$ is the room-temperature lateral (in-plane) film conductivity. $\beta$ and $\gamma$ are given by $S_i^{\mathrm{excess}} \propto i^{\beta}/f^{\gamma}$, where $S_i^{\mathrm{excess}}$ is the spectral density of the excess noise obtained by subtracting the thermal noise from the total noise of the sample. $i$ is the dc current flowing through the film, $f$ is the frequency. $\delta = S_i^{\mathrm{excess}} f/i^2$ is the dimensionless noise magnitude parameter.

| Sample | $N_l$ | $w$ (mm) | $d$ (mm) | $\sigma$ [a] (S/cm) | $\beta$ | $\gamma$ | $\delta$ [b] |
|---|---|---|---|---|---|---|---|
| 1 | 16 | 9.1 | 1.45 | $0.19 \pm 0.01$ | $1.97 \pm 0.04$ | $1.17 \pm 0.01$ | $(2.3 \pm 1.8) \times 10^{-10}$ |
| 2 | 46 | 9.0 | 1.15 | $0.16 \pm 0.01$ | $2.03 \pm 0.03$ | $1.15 \pm 0.01$ | $(2.4 \pm 1.4) \times 10^{-10}$ |
| 3 | 28 | 10.0 | 1.35 | $0.61 \pm 0.01$ | $2.00 \pm 0.03$ | $1.10 \pm 0.01$ | $(4.5 \pm 2.4) \times 10^{-11}$ |
| 4 | 28 | 9.0 | 1.45 | $0.57 \pm 0.01$ | $1.90 \pm 0.04$ | $1.20 \pm 0.01$ | $(7.0 \pm 2.9) \times 10^{-11}$ |

[a] $\sigma = 2d/(R_{\mathrm{sample}} h w N_l)$, where $R_{\mathrm{sample}}$ is the sample resistance, $h = 10$ Å (see Fig. 2).

[b] The large deviations of $\delta$ are connected with the variation of this parameter over the current and frequency ranges.

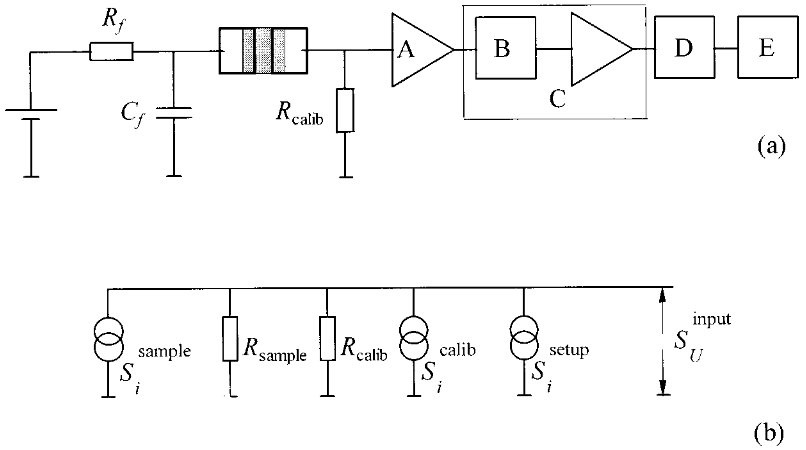

FIG. 4. (a) Schematic diagram of the experimental setup for the noise measurements: $A$, low-noise preamplifier; $B$, antialiasing filter; $C$, selective amplifier with variable band-pass filter; $D$, analog-to-digital converter; $E$, computer. $R_f=82.5\ \text{k}\Omega$, $C_f=200\ \mu\text{F}$, $R_{\text{calib}}=83.3\ \text{k}\Omega$. (b) The noise equivalent scheme of the experimental setup.

Figure 4(b) presents the noise equivalent scheme of the experimental setup. In this scheme, $S_i^{\text{sample}}$, $S_i^{\text{calib}}$, and $S_i^{\text{setup}}$ are the spectral densities of the noise current generators representing the noise of the sample, calibrated resistor and the total noise of the preamplifier and power supply, respectively. We define experimental spectral density of noise current as $S_i^{\text{input}}(f)=S_U^{\text{input}}(f)/R_{\text{equiv}}^2$, where $S_U^{\text{input}}$ is the spectral density of voltage fluctuations at the input of the low-noise preamplifier, $R_{\text{equiv}}=R_{\text{sample}}R_{\text{calib}}/(R_{\text{sample}}+R_{\text{calib}})$ is the resistance of the sample and calibrated resistor connected in parallel for the noise current.

As follows from the noise equivalent scheme, $S_i^{\text{input}}=S_i^{\text{sample}}+S_i^{\text{calib}}+S_i^{\text{setup}}$. In this expression, the noise of calibrated resistor $S_i^{\text{calib}}(f)$ is described by Nyquist's formula $S_i^{\text{calib}}=4k_BT/R_{\text{calib}}$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. In order to evaluate experimentally the noise of the setup $S_i^{\text{setup}}$, we performed control measurements with the sample replaced by a low-noise metal-film resistor with the same resistance. We found that spectral densities registered in experiments with the LB films exceeded the value of the spectral densities observed in the control experiment $S_i^{\text{contr}}$ by 1–3 orders of magnitude in the low-frequency range, and that $S_i^{\text{contr}}$ did not practically depend on current. So we concluded that the setup noise does not influence our experimental results over the whole frequency range and for all values of dc current flowing through the sample. We also found that the experimental spectral densities $S_i^{\text{input}}$ approached the sum of thermal noise of the sample and calibrated resistor $4k_BT(1/R_{\text{sample}}+1/R_{\text{calib}})$ in the high-frequency range. This fact proves the correctness of the calibration of our experimental setup.

The experiments reveal that the noise in conducting LB films can be separated naturally into two components: the first one is a current-independent thermal noise expressed by the Nyquist formula $S_i^{\text{therm}}=4k_BT/R_{\text{sample}}$, the second one—$S_i^{\text{excess}}=S_i^{\text{sample}}-S_i^{\text{therm}}$—increases with increase of the dc current flowing through the film and rises in the low-frequency range.

As follows from the noise equivalent scheme, $S_i^{\text{excess}}=S_i^{\text{input}}-S_i^{\text{contr}}$. The dependences $S_i^{\text{excess}}(f)$ for sample 4 at several values of dc current $i$ flowing through the film are shown in Fig. 5. It should be noted that it is possible to find $S_i^{\text{excess}}$ in this way with an admissible precision only in the range of frequencies and currents where $S_i^{\text{input}}(f)\gg S_i^{\text{contr}}(f)$. It determines the locations and lengths of frequency intervals for the curves in Fig. 5.

The spectral densities drawn in Fig. 5 can be approximated by a function $S_i^{\text{excess}}(f)\propto B/f^{\gamma}$, where $B=\text{const},\gamma\approx 1$; in other words, they represent the classical $1/f$ noise.

The inset of Fig. 5 shows the spectral densities $S_i^{\text{excess}}(i,f_0)$ at several fixed frequencies $f_0$ as functions of dc current $i$ flowing through sample 4. As it appears from this figure, $S_i^{\text{excess}}\propto i^{\beta}$, where $\beta\approx 2$. The fact that the noise power is approximately proportional to the square of the current and that the samples have a linear voltage-current characteristics over the current range used allows us to conclude that the $1/f$ noise in conducting LB films is caused by conductivity fluctuations.[5]

The measurements of spectral densities as a function of dc current and frequency in other samples (1–3) reveal similar results. The values of $\gamma$ and $\beta$ for all samples are listed in Table I.

The fact that the noise power spectral densities observed in the LB films are described by a power law $S_i^{\text{excess}}(f)\propto i^{\beta}/f^{\gamma}$, where $\beta\approx 2$ and $\gamma\approx 1$, allows us to use the relation $\delta=S_i^{\text{excess}}f/i^2$ as a dimensionless noise magnitude parameter. It is tabulated in Table I for all samples studied. Parameter $\delta$ depends (weakly) on current and frequency since the experimentally measured values of $\beta$ and $\gamma$ differ slightly from 2 and 1, respectively. Therefore, included in Table I the deviations of $\delta$ are not caused by errors in the noise power spectral density estimation but are connected with the variation of $\delta$ over the current and frequency range.

To determine where the noise originates (in the film or at the contacts) we studied how it depends on the number of charge carriers in the samples. In the case when the noise is caused by the contacts one should expect the noise magnitude to be independent of the number of charge carriers in the volume of the sample between the contacts. In the LB films studied the number of charge carriers $N_c$ contained in

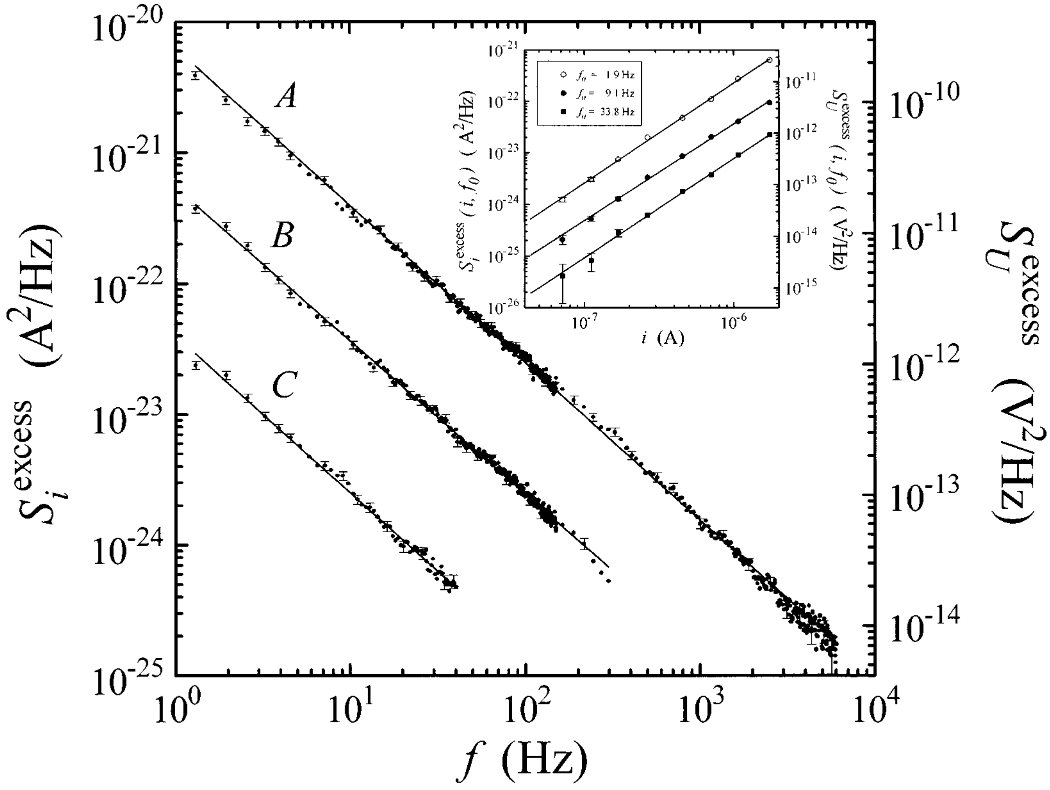

FIG. 5. The spectral densities of the excess noise $S_i^{\text{excess}}(f)=S_i^{\text{sample}}(f)-S_i^{\text{therm}}(f)$ obtained by subtracting the thermal noise from the total noise of sample 4 at several values of the dc current flowing through the sample (curves $A$–$C$, left-hand $Y$ axis): $A$, $i=4.3\ \mu\text{A}$; $B$, $i=1.1\ \mu\text{A}$; $C$, $i=0.3\ \mu\text{A}$. A least-squares fit to the dependences $S_i^{\text{excess}}(f)$ is the function $S_i^{\text{excess}}(f)\propto 1/f^{\gamma}$, where $\gamma=1.20\pm0.01$. In the inset, the spectral densities of the excess noise $S_i^{\text{excess}}$ at several frequencies $f_0$ as a function of dc current (left-hand $Y$ axis). A least-squares fit to the experimental points is the function $S_i^{\text{excess}}(i,f_0)\propto i^{\beta}$, where $\beta\approx1.9$. The frequencies $f_0$ are tabulated in the inset. Right-hand $Y$ axes: $S_U^{\text{excess}}=S_i^{\text{excess}}R_{\text{sample}}^2$, $R_{\text{sample}}=203.5\ \text{k}\Omega$.

the volume $V_{\text{cond}}=\frac{1}{2}hwN_ld$ [$V_{\text{cond}}$ is the volume of conducting part of the film (see Fig. 2)] may be estimated as $\sigma V_{\text{cond}}$. Indeed, since $\sigma=\mu ne$, then $\sigma V_{\text{cond}}=eN_c\mu$, where $n$ is the carrier concentration, $\mu$ is the carrier mobility, and $e$ is the electron charge. Figure 6 demonstrates the dependence of the noise magnitude $\delta$ on $\sigma V_{\text{cond}}$. A least-squares fit to the four points gives a slope of $-0.95$, not significantly different from $-1.0$. Hence, we obtain that $\delta\propto 1/(\sigma V_{\text{cond}})\propto 1/N_c$. The fact that there is some dependence of the noise magnitude on the number of charge carriers in the sample volume indicates the bulk nature of 1/$f$ noise in the samples and unambiguously points out that the noise is not caused by the contacts.

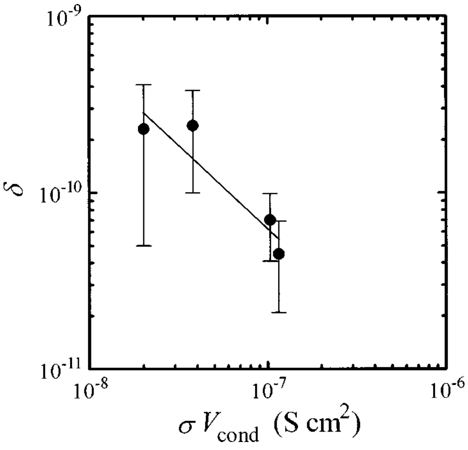

FIG. 6. Dependence of the dimensionless noise magnitude $\delta$ on $\sigma V_{\text{cond}}$. A least-squares fit to the four points gives the slope $-0.95$, not significantly different from $-1.0$.

## IV. DISCUSSION

### A. General

Fluctuations with spectral densities of the type $S(f,i)\propto i^2/f$ are the dominant kind of noise in the low-frequency range in metals and semiconductors.[5,6] Hooge[7] proposed the empirical formula for the 1/$f$ noise magnitude in a metal films, bulk semiconductors, and metals:

$$S_i^{\text{Hooge}}(f)=\frac{\alpha i^2}{N_c f},$$

where $N_c$ is the number of charge carriers and $\alpha\approx 2\times10^{-3}$ is the constant. Although this relation is not universally applicable, it can be used to provide a reasonable 1/$f$ noise order-of-magnitude estimations in many cases.

At present there is no theory for the origin of 1/$f$ noise in conducting LB films, so we compare the magnitude of the 1/$f$ noise derived for our LB films using the Hooge formula with our experimental results as the first step. Hooge's formula estimation gives

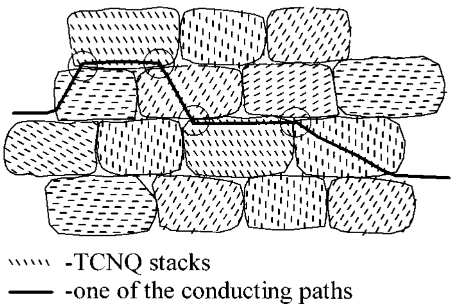

FIG. 7. Sketch of the simplified model for the charge propagation in LB films in plan view showing film crystallites and one of the conducting paths traced through TCNQ stacks. The nodes (conjunctions of stack ends) are in the circles.

$$\delta_{\rm Hooge}=\frac{S_i^{\rm Hooge}f}{i^2}=\frac{\alpha}{N_c}=\frac{\alpha}{nV_{\rm cond}}\approx 10^{-13},$$

where $n$ is the charge carrier concentration in the LB films (in our Hall-effect measurements[8] $n$ was found to be about $10^{17}$ cm$^{-3}$), $V_{\rm cond}=\frac{1}{2}hwN_ld$ is the volume of the conducting part of the film (see Fig. 2). As we can see, the experimentally measured values of $\delta$ listed in Table I are on average three orders of magnitude larger than the values obtained with the use of Hooge's formula. Because of the empirical character of Hooge's relation, this discrepancy is not surprising. It may point to differences of conduction mechanisms in LB films and those systems in which Hooge's formula works well. For this reason, in the next section we shall consider electron transport in LB films at the microscopic level.

### B. Model

As was shown in transmission electron microscopy and electron diffraction studies,[1] LB films of charge-transfer complexes consist of crystallites with size of the order of 1–10 $\mu$m. It is generally accepted that in these crystallites the head groups of constituting molecules (-TCNQ and -DMTTF) are gathered in separate stacks by analogy with that in bulk quasi-one-dimensional DMTTF-TCNQ crystals and that the charge propagates freely along the stacks inside.

To construct a model of the $1/f$ noise origin in conducting LB films and in polycrystalline quasi-one-dimensional crystals, one should consider in more detail the motion of charge in them.

Having reached the boundaries of crystallites, the charges tunnel through intercrystalline potential barriers from DMTTF or TCNQ stacks to the similar stacks located in the neighbor crystallites. Since the probability of such tunneling decreases exponentially with the increase of the distance, the probabilities of charge transfers to the nearest stacks will be larger than that to any of the other stacks by orders of magnitude. So, the motion of charge carriers in the film occurs by specific paths as shown schematically in Fig. 7. Let us term the place of conjunction of stack ends as the node (in Fig. 7 the nodes are in the circles). Due to the exponential dependence of the tunneling probability on the distance, thermal fluctuations of the potential barrier width in the node lead to large fluctuations of that probability, which in turn lead to the random switching of the corresponding paths between «on» and «off» states. Thus, in that model, fluctuations of conductances of single stacks are small as compared to fluctuations of node conductance and fluctuations of conductance of the sample are accounted for by fluctuations in the number of charge propagation paths.

The thermal fluctuations of distances between the stacks are caused by the influence of a large number of independent agents; so, the process of path switching with time obeys Poisson statistics. As a result, fluctuations in path conductance take the form of a random telegraph signal, which shows a relaxation-type (Lorentz-type) spectrum.[5] The spectrum of conductance fluctuations of the whole sample is the summation of the relaxation spectra of conductance fluctuations of single paths. The average time of functioning of a single path $\tau$ is a random variable in the ensemble of the sample paths with a distribution function $p(\tau)$ due to the polycrystalline nature of the samples. The shape of the distribution function $p(\tau)$ can be found from more detailed microscopic considerations. As was shown,[5,6] under some assumptions about the dependence $p(\tau)$, this sum can demonstrate a $1/f$ dependence over a limited range of frequency determined by the spread of the functioning times $\tau$. Thus, in principle, this model can explain the observed dependence of the spectral density of the conductance fluctuations on frequency: $S_G(f)/G^2=S_i(f)/i^2=\delta/f$, where $G$ is the sample conductance, and $\delta$ is the noise magnitude parameter, as defined above.

The model allows us to calculate the noise magnitude and thus to determine the value of parameter $\delta$. Let us denote conductance of a certain path by $g(t)$. Then $g(t_0)$ is a random variable that takes, with a probability of 0.5, either of these two values: $g$, when the conducting path is in the «on» state, and 0, when the path is in the «off» state. The dispersion of the random variable $g(t_0)$ is $\overline{(\Delta g)^2}=\overline{g(t_0)^2}-[\overline{g(t_0)}]^2=0.5g^2-(0.5g)^2=0.25g^2$ (the overbar in this expression denotes an averaging). The conductance of the sample with $N$ paths at the moment $t_0$ can be written in the form $G(t_0)=\Sigma_{k=1}^N g_k(t_0)$, where $g_k(t_0)$ is the conductance of the $k$th path. So, the average conductance of the whole sample is $G=\overline{G(t_0)}=\Sigma_{k=1}^N\overline{g_k(t_0)}=\frac{1}{2}\Sigma_{k=1}^N g_k$. Since $g_k(t_0)$ are independent random variables, the dispersion of the conductance of the whole sample is equal to the sum of the dispersions of $g_k(t_0)$, therefore $\overline{(\Delta G)^2}=\Sigma_{k=1}^N\overline{(\Delta g_k)^2}$. Taking into account this fact one can obtain

$$\frac{\overline{(\Delta G)^2}}{G^2}=\frac{\Sigma_{k=1}^N\overline{(\Delta g_k)^2}}{(\Sigma_{k=1}^N\overline{g_k})^2}=\frac{\Sigma_{k=1}^N g_k^2}{(\Sigma_{k=1}^N g_k)^2}=\frac{N\int_0^\infty g^2F(g)dg}{(N\int_0^\infty gF(g)dg)^2}=\frac{1}{N}\frac{\int_0^\infty g^2F(g)dg}{(\int_0^\infty gF(g)dg)^2}=\frac{C}{N}, \qquad (1)$$

where $F(g)$ is the distribution function of the path conductance [the value $N\,F(g)dg$ determines the number of paths with conductances in the range of $(g,\,g+dg)$].

It should be noted that Dubson *et al.*[9] obtained an estimation for the relative resistance noise of a two-dimensional random resistor network made up from identical resistors. This estimation has the form analogous to the Eq. (1), but there $N$ denotes the number of bonds that contribute significantly to the total noise.

In order to calculate constant $C$ in the Eq. (1), it is necessary to know the distribution function $F(g)$, which, in turn, may be found on the basis of microscopic consideration. To estimate $F(g)$ it is reasonable to assume the distances $l$ between the stack ends in the nodes to be a random variable distributed uniformly. Since, as was mentioned above, the probability of tunneling from one stack to another decreases exponentially with an increase of the distance, hence $g \propto \exp(-\kappa l)$, where $\kappa$ is a constant. Then assuming the conductance of the whole path to be determined by one node we obtain $F(g) \propto g^{-1}, g_{\min} \leqslant g \leqslant g_{\max}$. For this distribution function we have $C = \frac{1}{2} \ln(g_{\max}/g_{\min})$, i.e., for not too large ratio $g_{\max}/g_{\min}$ the value of $C$ is of the order of unity. So, performing estimations we shall suppose that $\overline{(\Delta G)^2}/G^2 = 1/N$.

$\overline{(\Delta G)^2}$ can be expressed also using the spectral density of the conductance fluctuations $S_G(f)$:[5]

$$\overline{(\Delta G)^2} = \int_{f_{\min}}^{f_{\max}} S_G(f)\,df = \delta\, G^2 \int_{f_{\min}}^{f_{\max}} df/f$$

$$= \delta G^2 \ln(f_{\max}/f_{\min}).$$

Therefore we have relations $\overline{(\Delta G)^2}/G^2 = 1/N$ and $\overline{(\Delta G)^2}/G^2 = \delta \ln(f_{\max}/f_{\min})$ from which we can find $\delta$.

The final expression for the noise magnitude parameter has the form

$$\delta_{\text{theor}} = \frac{S_i f}{i^2} = \frac{1}{N \ln(f_{\max}/f_{\min})}. \tag{2}$$

Formula (2) for the noise magnitude $\delta_{\text{theor}}$ involves the term $\ln(f_{\max}/f_{\min})$, where $f_{\max}$ and $f_{\min}$ are upper and lower limits, respectively, of the frequency range for $1/f$ noise. As was shown above, in our LB films $f_{\max}/f_{\min} = 10^4$ at least, so in our case $\ln(f_{\max}/f_{\min}) = \ln(10^4) \approx 9$. In general, $1/f$ noise can exist in a broader frequency range; however, the fact that $\delta_{\text{theor}}$ depends logarithmically on the $f_{\max}/f_{\min}$ leads to the weak variation of the expression (2) with expansion of the frequency range. For example, expansion of frequency range up to $10^{-6}-10^{6}$ Hz (the range in which $1/f$ noise was observed in other systems[5]) results in only triple decrease of $\delta_{\text{theor}}$. Therefore, even if we do not know the exact value of $f_{\max}/f_{\min}$, Eq. (2) gives a satisfactory estimation of the noise magnitude in polycrystalline quasi-one-dimensional systems.

### C. LB films: $1/f$ noise magnitude calculation

In order to evaluate the $1/f$ noise magnitude using formula (2), it is necessary to find the quantity of conducting paths in the film. This quantity can be estimated from the following simple considerations. As was mentioned above, the area per molecule $A$ in the monomolecular layer was about of 20 $\text{Å}^2 = 2 \times 10^{-15}$ cm$^2$. Since the area between the contacts can be expressed as $dw$ (see Fig. 3), the corresponding part of the monolayer contains $dw/A$ molecules.

As was shown in Ref. 8, the charge in our LB films propagates mainly along the TCNQ stacks. To form monolayers we used mixture $(C_{16}H_{33}\text{-TCNQ})_{0.4}(C_{17}H_{35}\text{-DMTTF})_{0.6}$, so the part of the monolayer between the contacts contained $0.4dw/A$ molecules $C_{16}H_{33}$-TCNQ. In the film crystallites the distance $\Delta$ between the neighbor TCNQ head groups in the stack is of the same order of magnitude as the similar distance in TTF-TCNQ crystals and amounts to about 3 Å $= 3 \times 10^{-8}$ cm. The length of a charge propagation path is of the order of the distance $d$ between the contacts, therefore one path contains $d/\Delta$ -TCNQ groups.

As follows from Fig. 7, there are TCNQ stacks through which the charge propagation path cannot be traced due to unfavorable location or orientation of them with respect to another stacks. In order to estimate the part of stacks involved in the process of conductivity we can use the fact that the system is similar to those considered in percolation theory[10] (the problem of conductivity in mixture of metallic and glass balls). It is known that percolation of current in such systems is possible only if the fraction of metallic balls is 30–40% at least. In the case of our system it means that, in order for the current to flow through the LB film, 30–40% of the stacks at least should be included in the conducting paths. Therefore for estimations we can suppose that *all* of the $0.4dw/A$ -TCNQ groups form the conducting paths.

Taking into account that the sample has $N_l$ of monolayers, the estimation of the number of paths in the sample is $N = 0.4N_l(w\Delta)/A$. This expression gives an upper bound for the number of the conducting paths. Substituting this estimation into Eq. (2) we obtain

$$\delta_{\text{theor}}^{\text{film}} = \frac{1}{N \ln(f_{\max}/f_{\min})} = \frac{A}{\ln(f_{\max}/f_{\min}) 0.4 w N_l \Delta}$$

$$= 4 \times 10^{-10} - 9 \times 10^{-10}. \tag{2$'$}$$

It is seen that $\delta_{\text{theor}}^{\text{film}}$ agrees within one order of magnitude with the experimental values of $\delta$ tabulated in Table I.

### D. TTF-TCNQ crystals: $1/f$ noise magnitude calculation

Above we repeatedly emphasized the similarity of the charge transport in the LB film crystallites and in the bulk TTF-TCNQ crystals. In this context it is interesting to compare their noise characteristics. $1/f$ noise measurements in TTF-TCNQ crystals were reported for the first time in Ref. 11. The temperature dependences of the normalized broadband (1–1000 Hz) excess noise power were presented in Fig. 11 of Ref. 11. At $T = 65$ K the value of this noise power ranges from $9 \times 10^{-12}$ to $9 \times 10^{-11}$. It is convenient to convert the normalized broadband excess noise power into the noise magnitude parameter $\delta$ introduced above. For this, the normalized broadband excess noise power should be divided by $\ln(1000) \approx 7$. Thus, we have $\delta_{\text{TTF-TCNQ}} \approx 1 \times 10^{-12} - 1 \times 10^{-11}$.

As in the case of the LB films let us compare the value of $\delta_{\text{TTF-TCNQ}}$ with that predicted by Hooge's formula. For this purpose it is necessary to find the number of charge carriers in TTF-TCNQ crystal. It can be done taking into account the following: (1) Parameters of the unit cell of TTF-TCNQ are[12] $a = 12.3$ Å, $b = 3.8$ Å, $c = 18.5$ Å, $\beta = 104.46°$, $V_0 = abc \sin\beta = 839.9$ Å$^3$. (2) Each unit cell contains two TCNQ molecules. (3) There are 0.6 conducting electrons per TCNQ molecule. Since the typical crystal dimensions are $2 \times 0.2 \times 0.03$ mm$^3$ ($V_{\text{cryst}} = 1.2 \times 10^{-5}$ cm$^3$), such a crystal contains $N_c = 2(V_{\text{cryst}}/V_0)0.6 \approx 1.7 \times 10^{16}$ charge carriers. Therefore the value of the $1/f$ noise magnitude parameter predicted by the Hooge formula is $\delta_{\mathrm{Hooge}}^{\mathrm{TTF\text{-}TCNQ}} = \alpha/N_c \approx 10^{-19}$. It is 7–8 orders of magnitude less than the experimentally observed $\delta_{\mathrm{TTF\text{-}TCNQ}}$. To our knowledge, this striking discrepancy has not been explained up to now.

Our model of $1/f$ noise origin can help to shed light on this problem. There is significant similarity between transport mechanisms in TTF-TCNQ crystals and conducting LB films. TTF-TCNQ crystal is the typical quasi-one-dimensional system. It is well known that charge carriers propagate mainly along the TCNQ stacks. Since the length of the stacks due to crystal imperfections is significantly less than the distance between the contacts, the charge carriers undergo multiple hops from stack to stack in the process of propagation. Therefore we can apply our model of the $1/f$ noise origin to TTF-TCNQ crystals. For this purpose it is necessary to estimate the number of charge propagation paths for the samples used in Ref. 11. It can be done taking into consideration the following circumstances: (1) In experiments with TTF-TCNQ crystals current flowed along the principal conducting $b$ axis. (2) The typical cross section of the samples of TTF-TCNQ across the $b$ axis of crystals is about $S \approx 10^{-4}$ cm$^2$. (3) The cross section of the unit cell across the $b$ axis is $ac \sin\beta$. (4) There are two TCNQ stacks per this cross section of the unit cell. Then the number of charge propagation paths is estimated as $N = 2S/(ac \sin\beta) \approx 9\times 10^9$. Substituting this value into Eq. (2) we obtain

$$\delta_{\mathrm{theor}}^{\mathrm{TTF\text{-}TCNQ}} = \frac{1}{N \ln(f_{\max}/f_{\min})} = \frac{ac \sin\beta}{2S \ln(f_{\max}/f_{\min})} \approx 10^{-11}, \tag{2''}$$

which lies close to the experimentally observed values of $\delta_{\mathrm{TTF\text{-}TCNQ}} = 1\times 10^{-12} - 1\times 10^{-11}$.

## V. CONCLUSIONS

In summary, we studied the electric noise in conducting LB films of $(C_{16}H_{33}\text{-TCNQ})_{0.4}(C_{17}H_{35}\text{-DMTTF})_{0.6}$ charge-transfer complex in the frequency range of $1-10^4$ Hz in the presence of the dc current. Excess $1/f$ noise (along with the usual thermal noise) was found. It was proved that the noise originates in the bulk of the film and is not related to the contacts. Square dependence of the spectral density of noise on dc current indicates that the noise is caused by fluctuations of the film conductivity.

All attempts to explain the observed noise magnitude using ordinary approaches for analysis of $1/f$ noise were unsuccessful. The Hooge formula predicts the magnitude of $1/f$ noise to be 1000–3000 times less than the experimental values. Moreover, in the well-known crystals of TTF-TCNQ there is an even larger discrepancy (7–8 orders of magnitude) between the experimental value of $1/f$ noise[11] and the Hooge formula prediction.

To explain the discrepancies, we proposed a theoretical model for the origin of the $1/f$ noise. According to this model, the noise observed in conducting LB films and TTF-TCNQ crystals is believed to originate from charge transport peculiarities related to the quasi-one-dimensional nature of these systems: charge carriers move along the paths whose number fluctuates, and that causes the noise. Using this model we derived relation (2) between the spectral density of $1/f$ noise and the number of charge propagation paths. The relation satisfactorily predicts the value of the $1/f$ noise in the conducting LB films and crystals of TTF-TCNQ.

Accordingly to formula (2) the value of the noise is determined mainly by the number of charge propagation paths. This result is important because it means that the high level of the $1/f$ noise in conducting LB films and TTF-TCNQ crystals is related closely to the quasi-one-dimensional nature of the conduction mechanism and the polycrystalline structure of these substances. So, the magnitude of the $1/f$ noise could be reduced if only we reduce the distance between the contacts below the crystallite size or increase the crystallite size above that distance. This fact should be taken into consideration in discussion about possible applications of the conducting LB films in ME devices.

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