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Variable-range hopping within a fluctuating potential landscape

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Abstract. The effect of temporal and spatial potential-energy fluctuations on low-temperature dark dc conductivity in disordered materials is considered. Analytical models are formulated to treat the variable-range hopping in a disordered system of localized states whose energies are subjected to $1/f$ temporal fluctuations. Long-range spatial potential fluctuations are described as a random distribution of intrinsic electric field. Temporal $1/f$ fluctuations are assumed either to be independent of carrier hopping or to be caused by the latter process. Both spatial and independent $1/f$ temporal fluctuations are shown to yield temperature dependences of the conductivity much weaker than those predicted by the Mott law. Self-sustaining $1/f$ temporal fluctuations caused by the carrier random walk lead to the crossover from Mott's $T^{-1/4}$ to $T^{-1/3}$ dependence with increasing temperature.

1. Introduction

Amorphous semiconductors are normally considered as isotropic and homogeneous systems for charge transport processes implying that the characteristic scale of the disorder is much shorter than both carrier jump distance and inelastic scattering length [1, 2]. However, the presence of randomly distributed and oriented molecular dipoles or charged defects may lead to a random distribution of the electrostatic potential [3] whose characteristic scale is much larger than either the jump distance in a disordered hopping system or the mean free path of delocalized carriers in materials with trap-modulated band transport. The concept of a random potential landscape is not an unusual one in disordered systems. It was used by Tauc [4] and Fritzsche [5] in their analysis of optical absorption in amorphous semiconductors. Overhof and Beyer [6] simulated the effect of long-range potential fluctuations on charge transport in disordered hopping systems. The occurrence of a random potential distribution was further suggested as a possible origin of the $\sqrt{F}$ field dependence of carrier mobility in disordered organic materials [7] and the suppressed rate of bimolecular recombination, experimentally observed in many amorphous materials, can also be explained by spatial separation of the electron and hole densities on the mesoscopic scale within a fluctuating potential landscape [8].

Moving the charges and/or rotating the dipoles which give rise to the random potential landscape must in any given material inevitably lead to interactions which give rise to temporal potential fluctuations. Although both the charge carrier random walk and the dipole rotation are slow processes at low temperatures they may generate low-frequency potential-energy fluctuations [9, 10] whose spectrum is quite different from the frequency spectrum of normal lattice oscillations which determine the temperature and participate in phonon-assisted processes. As far as carrier transport is concerned, the latter are revealed by electron–phonon

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interactions giving rise to thermally assisted carrier jumps while the former can (slowly) change the relative energy positions of starting and target states. Therefore, the random energy fluctuations will affect any process in which either carrier release from traps or charge transfer between localized states is involved.

Such fluctuations have been identified [11] as the origin of the apparent temperature dependence of the density-of-states energy distributions recovered from experimental photocurrent transients [12] or from modulated photocurrents [13, 14] in hydrogenated amorphous silicon (a-Si:H). The fluctuations result in early release of a localized carrier whenever it stays trapped long enough to undergo large-amplitude oscillations, implying a higher trap-controlled carrier mobility than could be expected without the fluctuations [15]. Photogeneration of charge carriers increases the density of charges whose diffusion enhances the random potential fluctuations. Concomitantly, localized carriers can be released from temporarily shallower traps that leads to an experimentally observed apparent upward shift of the trapping level in a-Si:H films under constant illumination [16]. In the present work we consider the effects of both temporal and spatial random potential-energy fluctuations on the low-temperature dark conductivity in disordered materials, *in casu* the variable-range hopping near the Fermi level. In the following sections we consider the effects of spatial and temporal fluctuations separately and we start our consideration with the former one.

2. Variable range hopping within a random potential landscape

Random potential fluctuations must give rise to a random distribution of local intrinsic electric field. If this field is strong enough to allow for carrier jumps without thermal activation, the temperature dependence of the dark conductivity may differ significantly from predictions of the standard variable-range hopping theory for a given density-of-states (DOS) distribution. In a random hopping system, an external field affects the conductivity mainly by changing the energy difference between starting and target sites. The rate, ν, of carrier jumps over the distance r between hopping sites of the energies E_s and E_t in the presence of the external field F is described by the Miller–Abrahams expression [17] that can be written in terms of a universal hopping parameter u defined as:

$$\nu = \nu_0 \exp(-u) \qquad u = 2\gamma r + \begin{cases} 0 & E_t < E_s + eFrz \\ \dfrac{E_t - E_s - eFrz}{kT} & E_t > E_s + eFrz \end{cases} \tag{1}$$

where $z = \cos\vartheta$, ϑ is the angle between the field and the jump direction, γ the inverse localization radius, T the temperature and k the Boltzmann constant. Following the Mott approach to the variable range hopping we consider carrier jumps from localized states with energies near the Fermi level, E_F, as the rate-limiting steps in the dark hopping conductivity. For a starting site located at the Fermi level, target sites, whose hopping parameters are less than u, may be found within the shaded area in figure 1. Assuming a constant density of states near E_F one may evaluate the average number of such target sites, $n(u, T, F)$ as

$$\begin{aligned} n(u,T,F) &= 2\pi g_0 \left[\int_0^1 \mathrm{d}z \int_0^{u/2\gamma} \mathrm{d}r\, r^2 \int_0^{kT(u-2\gamma r)+eFrz} \mathrm{d}E \right. \\ &\quad \left. + \int_{-1}^0 \mathrm{d}z \int_0^{kTu/2\gamma kT - eFr} \mathrm{d}r\, r^2 \int_0^{kT(u-2\gamma r)+eFrz} \mathrm{d}E \right] \\ &= \frac{\pi u^4}{3} \frac{g_0 kT}{(2\gamma)^3} \left[\frac{3f^3 + 8f^2 + 8f + 4}{4(1+f)^2} \right] \end{aligned} \tag{2}$$

where the dimensionless parameter $f = eF/2\gamma kT$ accounts for the field effect on the carrier hopping rate. The minimum value of u, sufficient to provide for dc conductivity, will be obtained when the average number of the target sites is sufficient to provide for a percolation path, i.e. when $n(u_{\min}, T, F) = n_c$. The use of this condition in equation (2) yields:

$$u_{\min} = \left(\frac{24 n_c \gamma^3}{\pi g_0 kT}\right)^{1/4} \left[\frac{4(1+f)^2}{3f^3 + 8f^2 + 8f + 4}\right]^{1/4}. \tag{3}$$

Concomitantly, neglecting weaker field and temperature dependences of the prefactor, σ_0, the conductivity, σ, can be written as

$$\sigma(F, T) = \sigma_0 \exp[-u_{\min}(F, T)]. \tag{4}$$

In a disordered system of charges, a Gaussian distribution function of variance F_0 may be considered as a fairly good representation of a random electric field:

$$\varphi(F) = \frac{1}{2\sqrt{\pi} F_0} \exp\left(-\frac{F^2}{F_0^2}\right). \tag{5}$$

In the absence of an external electric field, averaging of local microscopic currents yields zero macroscopic current:

$$\boldsymbol{j}(T) = \int \mathrm{d}\boldsymbol{F} \boldsymbol{F} \sigma(F, T) \varphi(F) \tag{6}$$

due to an isotropic distribution of the intrinsic electric field. However, if an external field $\boldsymbol{F}_{\text{ext}}$ is applied to the sample the field distribution is no longer isotropic, and a non-zero macroscopic current along the external field direction will result. Assuming that $F_{\text{ext}} \ll F_0$ and that $\boldsymbol{F}_{\text{ext}}$ is parallel to the z-axis of a Cartesian coordinate system the integral in the right-hand side of equation (6) yields:

$$\begin{aligned} j_z(T) &= \frac{1}{\pi^{3/2} F_0^3} \int_{-\infty}^{\infty} \mathrm{d}F_x \int_{-\infty}^{\infty} \mathrm{d}F_z F_z \sigma(F, T) \exp\left[-\frac{(\boldsymbol{F} - \boldsymbol{F}_{\text{ext}})^2}{F_0^2}\right] \\ &= \frac{8 F_{\text{ext}}}{3\sqrt{\pi} F_0^5} \int_0^{\infty} \mathrm{d}F\, F^4 \sigma(F, T) \exp\left(-\frac{F^2}{F_0^2}\right). \end{aligned} \tag{7}$$

Equation (7) shows that the average macroscopic conductivity, $\langle\sigma(T)\rangle$, of a hopping system with a Gaussian distribution of the intrinsic field is represented by the following expression:

$$\langle\sigma(T)\rangle = \frac{8}{3\sqrt{\pi} f_0^5} \int_0^{\infty} \mathrm{d}f\, f^4 \sigma(f, T) \exp\left(-\frac{f^2}{f_0^2}\right) \tag{8}$$

with the parameter f_0 being defined as $f_0 = eF_0/2\gamma kT$. At low temperatures, equation (8) predicts a very weak T-dependence of the dark conductivity in the presence of intrinsic field fluctuations, with the low-temperature limit of the conductivity being higher for stronger field fluctuations, i.e. at higher values of F_0. This lack of temperature dependence is caused by a dominant contribution to the conductivity of field-assisted carrier jumps within domains of sufficiently strong intrinsic field. It follows directly from equations (3) and (4) that the field-assisted conductivity does not depend upon T at low temperatures and reveals an $\exp[-(F_*/F)^{1/4}]$ dependence upon the local intrinsic field strength [18]:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{64 n_c \gamma^4}{\pi g_0 eF}\right)^{1/4}\right] \qquad \frac{eF}{2\gamma kT} \gg 1. \tag{9}$$

It is worth noting that the temperature at which the σ–T dependence levels off increases with increasing field. In other words, a crossover from the T-independent regime of field-assisted

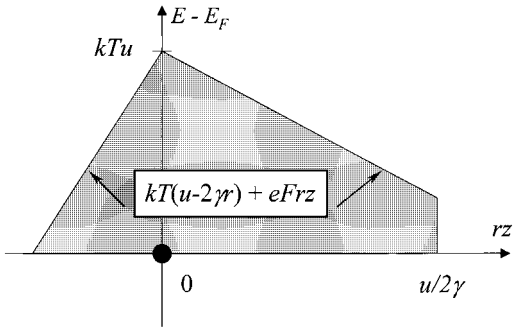

Figure 1. Region in the r–E space where neighbouring vacant sites of the hopping parameter less than u are located.

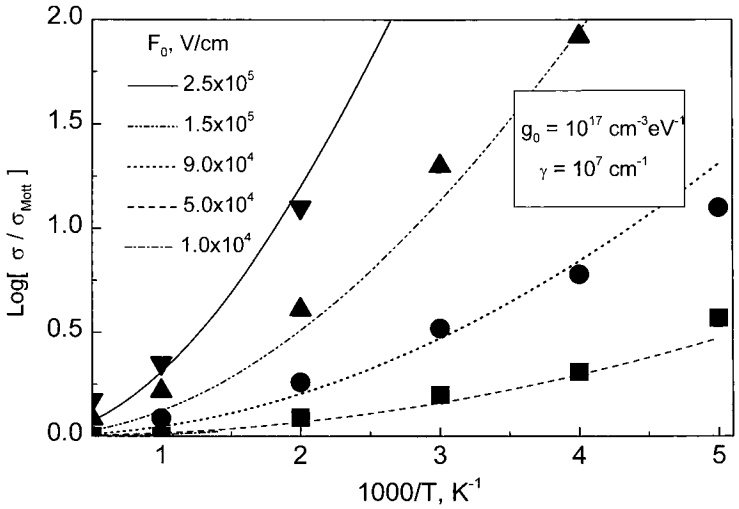

Figure 2. The effect of random potential fluctuations on the dc conductivity. The temperature dependence of the conductivity calculated from equation (7) is normalized to the Mott conductivity and compared with the results of Monte Carlo simulations of carrier hopping within a random potential landscape [3].

carrier jumps to the Mott $T^{-1/4}$ dependence occurs at higher temperatures in materials with stronger intrinsic field fluctuations.

Carrier transport in a random hopping system with long-range potential fluctuations was simulated by Overhof and Beyer [6]. The data obtained from this simulation are presented in figure 2 together with analytic results calculated from equation (8). Obviously, a good quantitative agreement is obtained with values for the variance of the Gaussian distribution of the intrinsic fields which are very realistic.

3. Variable-range hopping in a system with temporal fluctuations of hopping site energies

In a random system of energetically fluctuating hopping sites, the rate of carrier jumps will be determined by the interplay of potential fluctuations and of thermally assisted jumps between

states with temporarily fixed energies. At higher temperatures, a carrier can easily acquire sufficient thermal energy to make an upward jump from a starting site of the energy E_s to a target site of the energy E_t before the energy difference between the two sites, $E_t - E_s$ is noticeably changed in the course of potential fluctuations. On the premise of a constant DOS distribution near the Fermi level, $g(E) = g_0$, this leads to the famous Mott $T^{-1/4}$ law for the dark dc conductivity. However, in a disordered system, hopping rates may be low enough to allow for strong potential fluctuations before the jump is made and, therefore, for considerable changes in energies of nearest hopping neighbours compared to what should be expected without the fluctuations.

Random temporal potential fluctuations can be caused either by some charge relaxations independent of the variable-range hopping of carriers near the Fermi level or by redistribution of charge density caused by the VRH itself. In the former case, one may consider the fluctuations as an *ab initio* background on which the carrier transport occurs and neglect the effect of carrier transport jumps on the spectrum and the amplitude of the fluctuations. Under the latter circumstances, one must consider carrier transport and potential fluctuations as a self-consistent process without assuming any specific spectrum of the fluctuations in advance. In the following, we consider these two possibilities separately.

3.1. Background temporal fluctuations

In a random hopping system, a carrier localized in a hopping site of energy E_{st} normally has a well distinguished nearest hopping neighbour characterized by the smallest value of the hopping parameter u defined by equation (1) with $F = 0$. At a fixed value of u, all hopping neighbours with hopping parameters less than u of a site of the energy E_{st} above the Fermi level must be located within an area in energy-coordinate space, analogous to the one shown in figure 1 (but symmetric since $F = 0$). The number of such hopping neighbours, $n(u)$, increases with increasing u as

$$n(u) = 4\pi g_0 \int_0^{u/2\gamma} \mathrm{d}r\, r^2 \int_{E_r}^{E_{st}+kT(u-2\gamma r)} \mathrm{d}E = \frac{\pi g_0 kT}{24\gamma^3} u^4 \left(1 + 4\frac{E_{st} - E_F}{kTu}\right). \tag{10}$$

Since most carriers make jumps to nearest hopping neighbours, the minimum value of n that allows the occurrence of a carrier jump from an occupied state must be equal to one. Solving the equation $n(u_{tr}) = 1$ yields the critical value of the hopping parameter, u_{tr}, that is sufficient to provide for dc hopping conductivity $\sigma = \sigma_0(T)\exp[-u_{tr}(T)]$, where $\sigma_0(T)$ is the prefactor determined by the average jump distance at a given temperature. The use of the function $n(u)$ given by equation (10) leads to the following equation for the minimum hopping parameter:

$$u_{tr}^4 \left(1 + 4\frac{E_{st} - E_F}{kTu_{tr}}\right) = \frac{24\gamma^3}{\pi g_0 kT}. \tag{11}$$

Solving this equation for carriers making jumps from stable sites near the Fermi level, $E_{st} = E_F$, i.e. neglecting the fluctuations, yields the Mott-type expression for the critical transport value of the hopping parameter as

$$u_{tr}(T) = \left(\frac{24\gamma^3}{\pi g_0 kT}\right)^{1/4}. \tag{12}$$

To introduce the fluctuations into the formalism we use the fact that, although the fluctuating potential landscape affects energies of all hopping sites, for random oscillations this is equivalent to a fluctuating energy at the starting site, with energies of target sites being unchanged. The low-frequency tail of the random-fluctuation spectrum generally reveals a $1/f$ frequency dependence, $A \propto f_0/f$, with f_0 being the characteristic frequency of the

fluctuations, that implies a linear increase with time of the fluctuation amplitude A. Therefore, one could account for the random energy oscillations in equation (11) by assuming a linear time dependence of the starting-site energy: $E_{st}(t) = E_F + \Delta(T) f_0 t$, where Δ accounts for the temperature dependence of the fluctuation amplitude. If the fluctuations are not caused by carrier motion a linear temperature dependence for the amplitude, $\Delta(T) = kT$, should be acceptable, given the stronger exponential dependence upon temperature of the jump rate. This yields the following equation for the minimum hopping parameter,

$$u_{tr}^4(t)\left(1 + 4\frac{f_0 t}{u_{tr}(t)}\right) = \frac{24\gamma^3}{\pi g_0 kT} \tag{13}$$

whose solution now depends upon the relevant time scale. Since the time a carrier remains in the starting site will determine the longest time it can undergo the fluctuations (corresponding to the largest fluctuation amplitude), one must use the jump time $t_j = (1/\nu_0)\exp(u_{tr})$ as the relevant fluctuation time in the left-hand side of equation (13) that yields an implicit expression for the fluctuation-affected critical value of the hopping parameter:

$$u_{tr}^4\left[1 + 4\frac{f_0}{\nu_0 u_{tr}}\exp(u_{tr})\right] = \frac{24\gamma^3}{\pi g_0 kT}. \tag{14}$$

Neglecting the second term in the left-hand side of equation (14) of course yields the Mott-type expression for the minimum hopping parameter. This 'fluctuation' term remains small and, correspondingly, the Mott solution remains valid if the following condition is fulfilled:

$$4\frac{f_0}{\nu_0}\left(\frac{\pi g_0 kT}{24\gamma^3}\right)^{1/4}\exp\left(\frac{24\gamma^3}{\pi g_0 kT}\right)^{1/4} \ll 1. \tag{15}$$

The condition given by equation (15) can be met only at sufficiently high temperatures. At lower temperatures it is not valid, implying a dominant role of the energy fluctuations in the carrier transport processes. The use of a set of material parameters which is typical for amorphous semiconductors, $g_0 = 10^{18}$ cm^{-3} eV^{-1}, $\gamma = 10^7$ cm^{-1}, yields the crossover temperature $T_c \approx 40$ K for a ratio $f_0/\nu_0 = 10^{-15}$.

At lower temperatures, i.e. under the regime of fluctuation-controlled hopping, the conductivity reveals an almost linear dependence upon temperature:

$$\sigma = \sigma_0\left[\ln\left(\frac{6\gamma^3\nu_0}{\pi g_0 f_0 kT}\right)\right]^3\frac{\pi g_0 f_0 kT}{6\gamma^3\nu_0}. \tag{16}$$

In summary, the effect of random potential fluctuations with the fluctuation amplitude being proportional to temperature leads to a crossover from the Mott law at higher temperatures to a practically linear T-dependence of the conductivity at lower temperatures. This crossover is shown in figure 3 with the ratio f_0/ν_0 as a parameter.

3.2. Current-induced fluctuations

For fluctuations in the potential landscape due to the carrier jumps themselves one may assume that the fluctuation amplitude is proportional to the average jump rate, $\nu(T) \propto \nu_0\exp(-u_{tr})$, within the volume V where the Coulomb interaction of charge carriers is sufficiently strong, i.e. $\Delta(T) f_0 \propto \Delta_0 V kT g_0 \nu_0 \exp(-u_{tr})$, where the term $kT g_0$ accounts for the density of carriers which participate in the hopping near the Fermi level [16]. The use of this expression for the fluctuation amplitude in equation (13) yields the following equation for the minimum hopping parameter:

$$u_{tr}^4\left[1 + 4\frac{\Delta_0 V g_0}{u_{tr}}\right] = \frac{24\gamma^3}{\pi g_0 kT}. \tag{17}$$

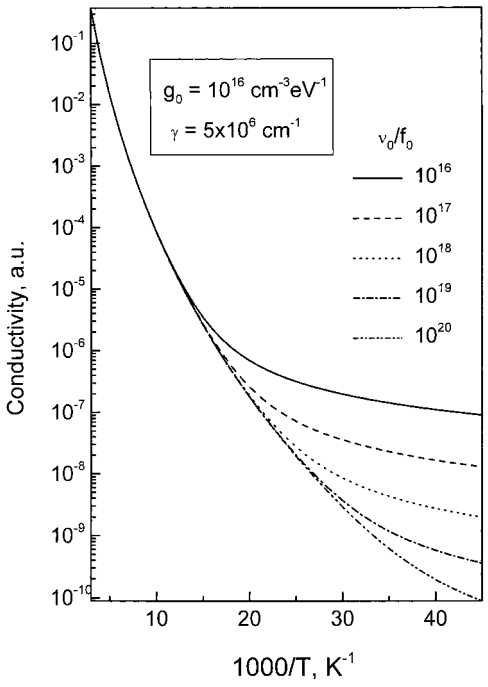

Figure 3. Temperature dependence of the conductivity controlled by the background temporal fluctuations of localized-state energies.

Equation (17) yields the Mott $T^{-1/4}$ dependence for the conductivity at *low* temperatures. At higher temperatures where the second term of the left-hand side of equation (24) becomes dominant, the T-dependence of σ changes from $T^{-1/4}$ to a $T^{-1/3}$ law:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{6\gamma^3}{\pi\Delta_0 V g_0^2 kT}\right)^{1/3}\right] \qquad T > \frac{3}{32\pi}\frac{\gamma^3}{kg_0(\Delta_0 V g_0)^4}. \tag{18}$$

As one can see from equation (18), the $T^{-1/3}$ law can be observed within a broad temperature interval in materials with high values of g_0 and $1/\gamma$ i.e. in strongly disordered and/or heavily doped materials. The temperature dependence of the conductivity affected by the self-sustaining potential fluctuations is illustrated in figure 4.

4. Discussion and conclusions

The occurrence of long-range spatial potential fluctuations implies either a random distribution of charged defects (normally, in inorganic materials) or a random distribution and/or orientation of molecular dipoles (mostly, in organic semiconductors). That these distributions cannot be constant in time follows from the observation that, if they were, the random potential landscape would be smoothed by redistribution of intrinsic charge carriers. Nevertheless, intrinsic charge carriers will try to compensate the random potential distribution and by their motion change it. Therefore, background spatial and temporal potential fluctuations must be coupled to each other.

Comparing equation (16) with equation (9) shows that accounting for both spatial and temporal background potential fluctuations yields T-dependences of the dark conductivity that either level off or become much weaker than predicted by the classical Mott theory at low temperatures. To our knowledge, such a weak temperature dependence of the conductivity is never experimentally observed in disordered materials. This implies that the amplitude of

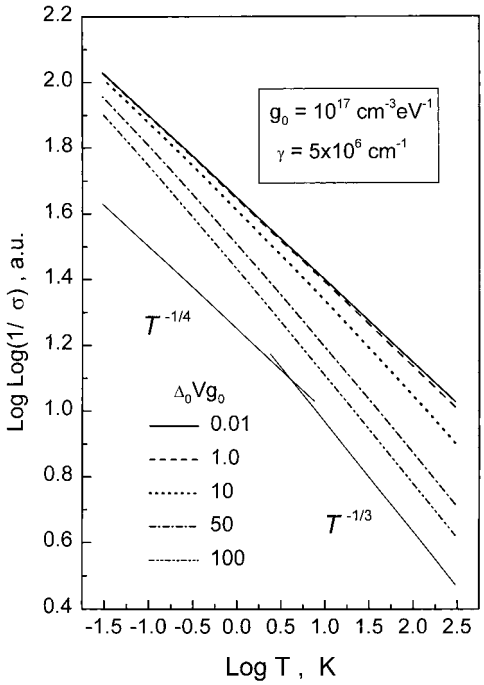

Figure 4. Temperature dependence of the conductivity controlled by the self-sustaining temporal fluctuations of localized-state energies.

the background fluctuations is strongly suppressed. This result is not really surprising since background fluctuations are assumed to be caused by some process that is slower than the carrier transport. In the present study that process is the variable-range hopping near the Fermi level, i.e. the slowest process which may give rise to redistribution of charge carriers in a structurally stable material. There is just no slower process that can be responsible for background fluctuations.

Nevertheless, a random walk of charge carriers near the Fermi level can still give rise to self-sustaining temporal potential fluctuations. The physical origin of such fluctuations is the Coulomb interaction between locally extrinsic travelling charge carriers with the surrounding electrons that occupy localized states around the Fermi level. In a sense, the model of carrier hopping controlled by self-sustaining potential fluctuations can be considered as a phenomenological approach to the problem of many-electron transitions in the variable-range hopping theory [19]. It is worth noting that the effect of such potential fluctuations on carrier hopping is not sensitive to the choice of a specific model of electron–electron interaction. A prominent feature of $1/f$ noise is that it describes the low-frequency limit of the fluctuation spectra independent of the process that causes these fluctuations. This universality implies the universality of T-dependence of hopping, controlled by $1/f$ potential fluctuations, irrespective of specific origin of these fluctuations. The $T^{-1/3}$ dependence of the dark dc conductivity was obtained assuming that the density of travelling carriers can be estimated as kTg_0 in accord with the one-particle Boltzmann distribution. However, many-electron self-assisting transitions may be equivalent to a higher effective temperature for one-particle excitations. Such processes should then lead to a weaker temperature dependence of the conductivity.

In conclusion, the only feasible mechanism of potential energy fluctuations at low temperatures is self-sustaining temporal fluctuations caused by carrier hopping near the Fermi level. Basically, introducing the concept of such fluctuations represents a phenomenological approach to the problem of many-electron excitations in the variable-range hopping in

amorphous materials. The obtained results prove that many-electron transitions may substantially change the temperature dependence of the dark dc conductivity within a broad temperature interval.

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References

[1] Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* 2nd edn (Oxford: Clarendon)
[2] Shklovskii B I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (Berlin: Springer)
[3] Overhof H and Thomas P 1989 *Electronic Transport in Hydrogenated Amorphous Semiconductors* (Berlin: Springer)
[4] Tauc J 1970 *Mater. Res. Bull.* **5** 721
[5] Fritzsche H 1971 *J. Non-Cryst. Solids* **6** 49
[6] Overhof H and Beyer 1981 *Phil. Mag.* B **43** 433
[7] Dunlap D H, Parris P E and Kenkre V M 1996 *Phys. Rev. Lett.* **77** 542
[8] Adriaenssens G J and Arkhipov V I 1997 *Solid State Commun.* **103** 541
[9] Ngai K L and Liu F-S 1981 *Phys. Rev.* B **24** 1049
[10] Drabold D A, Fedders P A, Klemm S and Sankey O F 1991 *Phys. Rev. Lett.* **67** 2179
[11] Arkhipov V I, Adriaenssens G J and Yan B 1996 *Solid State Commun.* **100** 471
[12] Yan B and Adriaenssens G J 1995 *J. Appl. Phys.* **77** 5661
[13] Schumm G, Nitsch K, Schubert M B and Bauer G H 1988 *Mater. Res. Soc. Symp. Proc.* vol 118 (Pittsburgh, PA: Materials Research Society) p 543
[14] Zhong F and Cohen J D 1992 *Mater. Res. Soc. Symp. Proc.* vol 258 (Pittsburgh, PA: Materials Research Society) p 813
[15] Arkhipov V I and Adriaenssens G J 1996 *Phil. Mag. Lett.* **73** 263
[16] Arkhipov V I and Adriaenssens G J 1996 *Phys. Rev.* B **54** 16 696
[17] Miller A and Abrahams E 1960 *Phys. Rev.* **120** 745
[18] Shklovskii B I 1973 *Sov. Phys.–Semicond.* **6** 1053
Shklovskii B I 1973 *Sov. Phys.–Semicond.* **6** 1964
[19] Davies J H 1985 *Phil. Mag.* B **52** 511