Theory of Space Charge Limited Currents

X.-G. Zhang and Sokrates T. Pantelides

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Theory of space charge limited currents

X.-G. Zhang[1,2] and Sokrates T. Pantelides[3,4]
[1]*Center for Nanophase Materials Sciences,*
[2]*Computer Science and Mathematics Division,*
[3]*Materials Science and Technology Division,*
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6493
[4]*Department of Physics and Astronomy,*
Department of Electrical Engineering and Computer Science,
Vanderbilt University, Nashville, TN 37235

Space-charge-limited currents are important in energy devices such as solar cells and light-emitting diodes, but the available theory from the 1950's finds it necessary to postulate defect states that are distributed in energy in order to match data. Here we show that this postulate is not warranted. Instead, we demonstrate that dopants and the concomitant Frenkel effect, which have been neglected, control the shape of measured current-voltage characteristics. We also account for the observed peak in the noise power. The new theory can anchor efforts to develop experimental techniques to measure deep-trap levels.

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Energy-conversion devices such as solar cells and light-emitting diodes rely on carrier injection, whose uncompensated charge and the concomitant push-back electrostatic field give rise to space-charge-limited currents (SCLCs). [1–5] For defect-free semiconductors, such currents were predicted to exibited a quadratic dependence on the voltage by Mott and Gurney. [6] Early data, however, [7, 8] however, exhibited an initial slow rise followed by a sharp, power-law rise at a critical voltage V_0, with the Mott-Gurney limit attained asymptotically. Rose [8] viewed the slow rise as an Ohmic current by available carriers and attributed the sharp rise to deep-level defects: injected carriers get trapped and generate a push-back voltage until all traps are filled (trap-filled limit or TFL); at the TFL, the push-back voltage is overcome and the current rises vertically. The Mott-Gurney limit is approached at higher voltages when the traps have no further effect. In developing a pertinent theory, Rose and later Lampert [9, 10] concluded that the only way to get a power-law instead of vertical rise in the current is to postulate an exponential tail of defect density of states (DOS). Since then, data are typically fitted piecemeal in the three regions, yielding limited useful information. In 2005, measurements of noise power spetrum in organic semiconductors [11] found a peak at the TFL that cannot be explained by the Lampert theory. Very recently, it was demonstrated [13] that the presence of dopants can have a large effect on SCLC's because dopant electrons can fill the deep traps, but a pertinent theory is lacking. For undoped materials, a Gaussian distribution of defect states was proposed [14] as an alternative to the exponential tail.

In this Letter, we demonstrate that the full inclusion of dopants and the *interplay between dopants and traps, which controls the power-law rise*, remove the need to postulate an exponential or Gaussian defect DOS (such disributions may of course exist in materials like polymers). The underlying physics is simple and elegant. Dopant energy levels are by definition above the trap levels. Because dopant densities must be smaller than those of the deep traps for SCLCs to occur, [12] most dopant electrons initially occupy trap levels, whereby *the Ohmic rise is controlled by thermal excitation from the deep traps*. The sharp rise is initiated when all deep traps are filled, as much as is allowed by local thermal equilibration, but the dopant levels are now a mitigating effect: the power-law rise is controlled by the dopant energy level [13] and the Frenkel effect, [15] namely the lowering of the ionization energy by the electric field, which is screened by the free carriers. [16] The power-law rise is finished when all traps *and* dopants are filled, as allowed by thermal equilibration, and is followed by the Mott-Gurney regime. For samples with high trap densities, trap-to-dopant hops may dominate the initial Ohmic-like rise of the current, suppressing the noise power at low voltages. [11] The detailed derivation, parameters for fitting experiments, and a FORTRAN code, are provided in the Supplemental Material.

The basic elements of the theory are quite simple. We consider a homogeneous material with concentrations N_D of donors and N_t of deep traps with $N_t > N_D$. At a given temperature T and external voltage V, the elecrostatic potential ϕ obeys the Poisson equation,

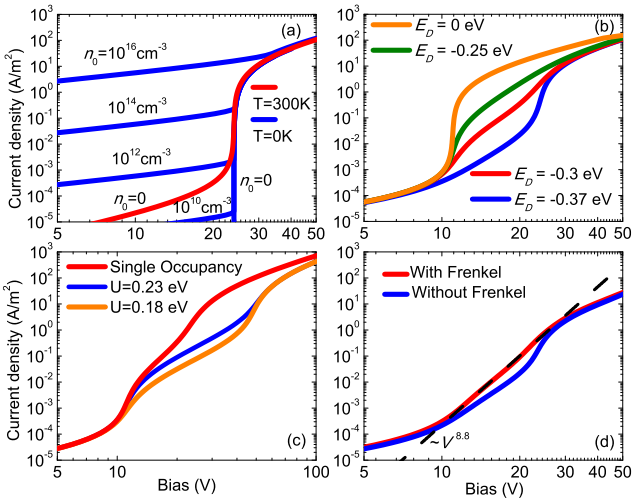
$$\nabla^2\phi = -\frac{e}{\epsilon\epsilon_0}(n + n_t - N_D^+ - p), \tag{1}$$

where n is the electron carrier density, n_t is the density of trapped electrons, N_D^+ is the density of ionized donors, and p is the free hole density; the electron current is,

$$J_n = \mu_n \left(en\mathcal{E} + kT\nabla n\right), \tag{2}$$

where $\mathcal{E} = -\nabla\phi$, and μ_n is the electron mobility, which depends on n, N_D^+, and T. All quantities except T and J depend on position x, and $\int_0^L \mathcal{E}(x)dx = V$, where L is the length of the sample. There is a corresponding equation for the hole current and the relation $np = n_i^2$, where n_i is the intrinsic density, whereby n is the only independent variable. Assuming thermal equilibration at each voltage, one can derive expressions for n_t and N_D^+ in terms of n (see below), whereby Eqs. (1) and (2) are coupled equations in ϕ and n. For each choice of J, they can be solved and yield the corresponding V for a current-voltage curve.

FIG. 1: Comparing the roles of dopant and trap level configurations for a model system. (a) Lampert model in which n_0 is an independent parameter, with a single trap level at $E_c - 0.5$ eV; (b) $E_t = E_c - 0.5$ eV with single occupancy and different dopant energy levels; (c) single and double occupancies with different values of on-site Coulomb energy U, $E_t = E_c - 0.5$ eV and $E_D = E_c - 0.3$ eV; (d) $E_t = E_c - 0.5$ eV, $U = 0.33$ eV, and $E_D = E_c - 0.37$ eV. (b)-(d) have a self-consistent N_D^+ instead of n_0.



We will demonstrate that the above constitutes a comprehensive theory of SCLCs. First, however, we identify the reason that Rose and subsequently Lampert were led to a dead end and had to postulate an exponential defect DOS. In their theory, $N_D^+(x) + p(x)$, which is equal to the part of the electron density whose charge is compensated, is set to the density of free carriers n_0 at zero voltage and treated as a fitting parameter. Though N_D^+ and p are constant at zero voltage, as electrons are injected into the material, they acquire a dependence on x and *their values get reduced as the voltage increases*. This reduction in N_D^+ is responsible for converting the would-be vertical rise of the current into a gradual power-law rise.

The main features of Lampert's theory is highlighted in Fig. 1a by replacing $N_D^+(x) + p(x)$ by a constant n_0 in Eq. (1) instead of using the thermodynamic expression to be presented shortly, and numerically solving the coupled Eqs. (1) and (2) for a model system with $L = 310$ nm and $N_t = 8.3 \times 10^{16}$ cm^{-3}. The results are as obtained by Rose and by Lampert, with a *vertical rise* at a critical voltage $V_0 = 24$ V, followed by the Mott-Gurney V^2 law. Also shown in Fig. 1a is the Ohmic rise (blue lines), calculated *separately* as in Lampert's theory, for several values of n_0. In the absence of free carriers other than those that are injected (effectively $T = 0$ K), one gets V_0 at [10]

$$V_0 = \frac{eN_tL^2}{2\epsilon\epsilon_0}. \tag{3}$$

If one allows thermal excitation from the deep traps at a finite temperature, one gets the *nonlinear* rise shown in red before reaching the vertical rise (often called the modified Mott-Gurney regime).

We now illustrate the main features and the inherent power of the comprehensive theory based on Eqs. (1) and (2). The other key equations are the expressions for n_t and N_D^+. We allow for the possibility that a given defect may have two trapping levels corresponding to a singly and doubly negative charged state, respectively (e.g., vacancies). [17–20] The second trap level is raised by the onsite Coulomb energy U, which we treat as a fitting parameter. We get,

$$n_t = \frac{g_1 N_t n N_c \exp(-E_1/kT)}{N_c^2 + g_1 n N_c \exp(-E_1/kT) + g_2 n^2 \exp(-E_2/kT)} + \frac{2g_2 N_t n^2 \exp(-E_2/kT)}{N_c^2 + g_1 n N_c \exp(-E_1/kT) + g_2 n^2 \exp(-E_2/kT)} \tag{4}$$

where g_1 and g_2 are degeneracy factors, N_c is the effective conduction band DOS [21] and E_1 is the effective trap level for single occupancy given by

$$E_1 = E_t - E_c + \delta E^{Fr} + \delta E_1^{Scr}, \tag{5}$$

and E_2 is the effective trap level for double occupancy,

$$E_2 = 2(E_t - E_c) + U + \delta E^{Fr} + \delta E_2^{Scr}. \tag{6}$$

The density of donor ions N_D^+ is related to the free carrier density n and the dopant energy level E_D through

$$N_D^+ = \frac{N_D N_c \exp[(E_D + \delta E_1^{Fr} + \delta E_1^{Scr} - E_c)/kT]}{n + N_c \exp[(E_D + \delta E_1^{Fr} + \delta E_1^{Scr} - E_c)/kT]}. \tag{7}$$

The corrections to the energy levels include a shift due to the Frenkel effect for a screened Coulomb potential,

$$\delta E_1^{Fr} \approx -\frac{4.2e\mathcal{E}\lambda - kT\ln(1 + 4.2e\mathcal{E}\lambda/kT)}{1 + 4.2\sqrt{4\pi\epsilon\epsilon_0\mathcal{E}/e\lambda}}, \tag{8}$$

which is an approximation of the exact numerical solution, where the Debye screening length is given by $\lambda = \sqrt{\epsilon\epsilon_0 kT/(e^2 n)}$, or the Frenkel effect for a neutral trap,

$$\delta E^{Fr} = -kT\ln\left\{\frac{1}{2} + \frac{kT}{2\mathcal{E}a}\left[1 - \exp\left(-\frac{\mathcal{E}a}{kT}\right)\right]\right\}, \tag{9}$$

and shift due to the screening charge around an ion site,

$$\delta E_n^{Scr} = \pm\frac{n^2e^2}{4\pi\epsilon\epsilon_0\lambda}, \tag{10}$$

where the $+$ sign is for dopant energy levels, the $-$ sign is for trap energy levels, and n is the number of charges on the site (the Frenkel effect was not considered in Lambert's theory).

The final set of equations is the temperature dependence of the carrier mobility. [23] The total mobility is given by

$$\frac{1}{\mu_n} = \frac{1}{\bar{\mu}_{ii}} + \frac{1}{\bar{\mu}_{op}} + \frac{1}{\bar{\mu}_{ac}}, \tag{11}$$

where the three contributions are charged-impurity, optical-phonon, and acoustic-phonon scattering, respectively. The

mobilities depend on the screening length λ, which in turn is a nonlinear function of the mobility through the free carrier density n.

The key difference between the full solution and prior theory is the inclusion of the dopant ions, N_D^+, in Eq. (1). Because N_D^+ has opposite charge from N_t, the turn-on voltage is reduced from Eq. (3) to

$$V_c = \frac{e(N_t - N_D^+)L^2}{2\epsilon\epsilon_0}. \tag{12}$$

As the dopant sites are filled by injected carriers, N_D^+ decreases with the applied voltage, resulting in a much more gradual increase of the current density. The dramatic effect of dopants is demonstrated in panels b through d of Fig. 1. In Fig. 1b, we show the I-V curves for a single trap at $E_c - 0.5$ eV plus dopants (with $N_D = 4.5 \times 10^{16}$ cm^{-3}) for several values of dopant energy E_D from 0 to 0.37 eV below E_c. These curves are calculated without inclusion of the Frenkel effect. We note that carriers from the dopants provide an initial Ohmic rise, while the interplay between the dopants and the traps slants the vertical rise in a significant way. The slanted rise, however, does not have the smooth power law observed in most experiments.

In Fig. 1c we compare results for traps that have either one or two occupancies (negatively charged and doubly negatively charged). The three curves correspond to single occupancy and double occupancies with $U = 0.23$ eV and 0.18 eV, respectively. These curves are also without the Frenkel effect. One feature of the double occupancy of traps is the appearance of a wide "modified Mott-Gurney" regime between two sharp rises corresponding to $N_t - N_D$ and $2N_t$, respectively. The sharp rise at N_t disappears when there is double occupancy.

Inclusion of the Frenkel effect is not optional, its significance shown in Fig. 1d. It is clear that the Frenkel effect, mostly on the dopants with a Coulombic potential, plays an important role: it straightens the slanted rise into a power law (the dashed black line is a pure power law and is inserted as a guide to the eye). The net conclusion is that *it takes a self-consistent solution of the coupled equations that govern the occupancy of both the dopants and the traps, including the Frenkel effect and multiple occupancies, to get a complete theory that generically has the observed behavior.*

The last ingredient of the theory is a tunneling current that may be present in materials with very high defect and dopant concentrations. The tunneling current between trap sites is usually considered negligible because of the large distance between traps. However, when both the deep traps and the shallower dopants exist in large concentrations, an electron in a deep trap can undergo thermally activated tunneling to a dopant level similar to variable range hopping [24, 25]. Likewise, an electron in the shallow trap can tunnel into a deep trap. In the presence of an electric field, such tunneling is biased and contributes to the current. Equation (2) is then modified to include this contribution,

$$J_n = \mu_n \left(en\mathcal{E} + kT\nabla n\right) + e\mu_t n_{tD}\mathcal{E}, \tag{13}$$

where $n_{tD} = N_t f(E_t)[1 - f(E_D)]$ is an effective carrier density. μ_t is an effective mobility for trapped carriers,

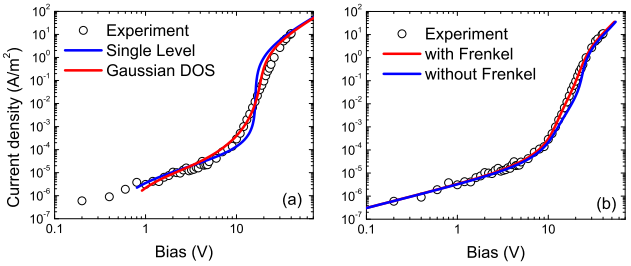


FIG. 2: Comparing the I-V data with theory for an electron-only PPV device [26], (a) best fits using the Lampert theory with a single trap level (blue) and a Gaussian defect DOS (red) with a smearing of 0.1 eV; (b) present theory including the Frenkel effect (red), and neglecting the Frenkel effect (blue).

$$\mu_t = \frac{ed}{4kT}\nu \exp[(E_t - E_D)/kT], \tag{14}$$

where d is the average distance between a deep trap site and a dopant site, and the hopping rate $\nu = \nu_0 \exp(-2d\sqrt{-2mE_D/\hbar})$ containing the attempt rate ν_0 which is assumed to be the typical phonon frequency and the tunneling rate obtained from simple tunneling.

We now demonstrate the power of the new theory by applying it to fit and interpret available data. In Fig. 2 we compare experimental data [26] on poly(phenylene vinylene), PPV, with the best fits using the Lampert theory with a single trap or with a Gaussian defect DOS (with a fitted smearing of 0.1 eV) in panel a, and using the present theory in panel b. In Fig. 2a, it is clear that a single trap energy level cannot account for the data. A Gaussian smeared defect DOS improves the fit significantly, but a deviation from the experimental curve is evident at high voltages. Furthermore, the attempt to incorporate an intrinsic carrier density ρ_0 without introducing a dopant density N_D leads to a highly nonlinear "Ohmic" regime. Blom et al. [26] fitted the initial rise of their data with an Ohmic current and the power-law rise with Lampert's theory assuming an exponential defect DOS. Their fit yielded a trap density $N_t = 5 \times 10^{17}$ cm^{-3}. Using this value, one can use Eq. (3) for the critical field V_0 to get $V_0 = 145$ V, whereas the data exhibit a turn-on voltage at ~ 9 V and a switch to the Mott-Gurney limit at ~ 20 V. We emphasize that in Ref. 26, the Ohmic rise was fitted by an independent theory of free carriers from dopants, with the density of free carriers being an adjustable parameter. The Gaussian defect DOS model [14] did not resolve this issue.

Using the present theory, we are able to fit the experimental curve with a single species of traps with two occupancies and no tunneling current. The Frenkel effect for the dopants plays a major role in fitting the data. To demonstrate that the fit represents internally consistent physics we examine two critical voltages. The first corresponds to all the trap sites being filled but the dopant sites, which have a higher energy level, are still quite empty. That is the nominal TFL turn-on voltage

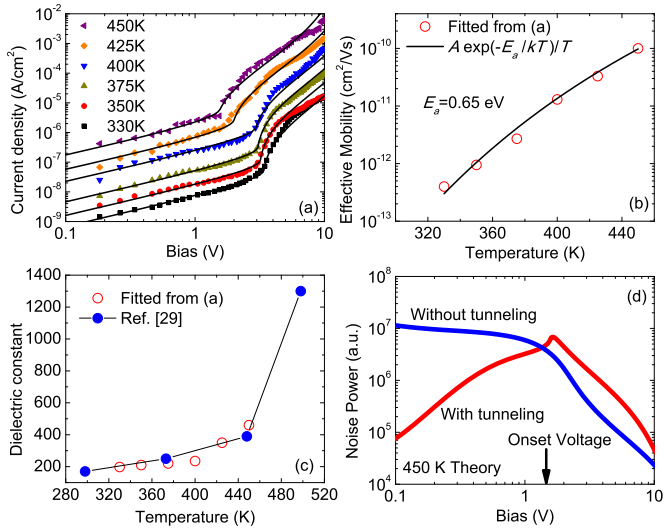


FIG. 3: Fits for a $SrBi_2Ta_2O_9$ polycrystalline film [28]. (a) Solid curves are fits using a temperature dependent dielectric constant ϵ; (b) effective mobility for the tunneling current in the Ohmic regime as a function of temperature; (c) temperature dependence of the fitted ϵ (open red circles), the filled blue circles are from Ref. 29; (d) noise power using two sets of parameters, with (red) and without (blue) inter-trap tunneling current. The parameters without tunneling can only fit 450 K but not other temperatures.

at $T = 0$ K and is given by Eq. (12). Using the values of $N_t = 8.1 \times 10^{16}$ cm^{-3} and $N_D = 4.4 \times 10^{16}$ cm^{-3} extracted from the fit, we find $V_c = 11$ V, in agreement with the data. The second voltage of interest, given by Eq. (3), is when the TFL curve turns over into the Mott-Gurney law. From the fitted N_t, Eq. (3) yields $V_{\rm TFL} = 24$ V, also in agreement with Fig. 2.

It is clear that *within the TFL region the injected carriers are filling the dopant sites*. Thus, the slope of the I-V curve in the TFL region is determined by the dopant concentration. Furthermore, *higher dopant concentration leads to a smaller turn-on voltage*. This feature has been observed, [13, 27] but has not been properly accounted for in the SCLC theory.

The Frenkel effect is crucial for the appearance of a power-law rise at the TFL. When the dielectric constant of the material is large, the Frenkel effect is diminished by screening, and the the I-V curves do not exhibit a straight power-law rise. One such example is the set of temperature-dependent data measured for a $SrBi_2Ta_2O_9$ polycrystalline film [28] which shows a strong temperature-dependent TFL region and onset voltage. These data offer an opportunity to test the temperature dependence of SCLCs predicted by the present theory.

Figure 3a shows a fit of the above data using the present theory. The fit is quite satisfactory. In this case, the initial Ohmic-like rise is dominated by the tunneling current and is not exactly linear, with an activation energy, extracted from the mobility plot in Fig. 3b, equal to the trap-to-dopant energy-level difference. The consistency of the fit is also demonstrated in Fig. 3c, where the temperature dependence of the fitted dielectric constant is compared to another experiment [29].

To further corroborate the presence of tunneling currents, we consider the voltage dependence of the noise power. Although Ref. 28 did not measure this, other measurements of samples exhibiting SCLC indicate that the noise power peaks slightly above the onset voltage [11]. Without the tunneling current between traps and dopant sites, the noise power is high and approximately constant at low voltages, as shown by the blue curve in Fig. 3d. The noise is significantly suppressed if the tunneling current dominates the Ohmic regime, shown as the red curve in Fig. 3d.

In conclusion, we have shown that a proper SCLC theory can be formulated only if the interplay between dopants and deep traps is considered and the Frenkel effect is included. Recognition of the role of dopants in the SCLC phenomenon allows the possible realization of Rose's vision of using the SCLC to probe deep-trap levels in semiconductors and insulators. In particular, one can design experiments with various concentrations of dopants, to "stretch" the TFL region to different voltage ranges in order to provide multiple curves for the study of a single deep trap level. Noise power measurements are useful for identifying the nature of the diffusive current at low voltages.

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