Validity of the Einstein Relation in Disordered Organic Semiconductors

G. A. H. Wetzelaer,[1,2] L. J. A. Koster,[1] and P. W. M. Blom[1,3]

[1]*Molecular Electronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

[2]*Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands*

[3]*TNO/Holst Centre, High Tech Campus 31, 5605 KN Eindhoven, The Netherlands*

(Received 18 April 2011; published 4 August 2011)

It is controversial whether energetic disorder in semiconductors is already sufficient to violate the classical Einstein relation, even in the case of thermal equilibrium. We demonstrate that the Einstein relation is violated only under nonequilibrium conditions due to deeply trapped carriers, as in diffusion-driven current measurements on organic single-carrier diodes. Removal of these deeply trapped carriers by recombination unambiguously proves the validity of the Einstein relation in disordered semiconductors in thermal (quasi)equilibrium.

DOI: 10.1103/PhysRevLett.107.066605 PACS numbers: 72.80.Le, 72.80.Ng, 73.40.Sx, 73.50.Gr

Fundamental for charge transport in semiconductors is the ratio between diffusivity and mobility, characterized by the classical Einstein relation [1]

$$\frac{D}{\mu} = \frac{kT}{q}, \tag{1}$$

with D the diffusion coefficient, μ the charge carrier mobility, k the Boltzmann constant, T the temperature, and q the elementary charge. However, the validity of this relation in disordered materials, such as organic semiconductors, is nontrivial. As charge transport in these disordered semiconducting systems is generally characterized by a hopping process between localized sites in a Gaussian or exponential density of states (DOS) distribution [2–4], their physical properties deviate significantly from classical semiconductor models. Therefore, the applicability of the Einstein relation to disordered semiconductors has been a matter of intensive research, where it is important to distinguish between equilibrium and nonequilibrium effects. Because of large disorder, the time for carriers to equilibrate can be very large, so that nonequilibrium transport is not uncommon in disordered semiconductors. Numerous theoretical and experimental studies [5–8] concluded that the Einstein relation is violated under nonequilibrium conditions, mainly due to the electric field dependence of the diffusivity being larger than the field response of the mobility. However, even under quasiequilibrium conditions, it has been proposed that Eq. (1) does not hold for disordered semiconductors [9–11]. This has been attributed to their nonclassical DOS distributions, requiring the application of an Einstein relation generalized for an arbitrary energy-distribution function of charge density and localized states. The DOS of organic semiconductors is generally described by a Gaussian energy distribution, for which the generalized Einstein relation is expressed as [10]

$$\frac{D}{\mu} = \frac{p}{q\frac{\partial p}{\partial E_f}} = g(p,T)\frac{kT}{q}, \tag{2}$$

where p is the charge carrier density and E_f the quasi-Fermi level. The factor $g(p,T)$ can be regarded as a dimensionless enhancement function of the classical Einstein relation that follows from the DOS variance σ. As a result, the Einstein relation becomes charge-density- and temperature-dependent, with g increasing for increasing density and decreasing temperature. However, even though such a derivation is commonly accepted, Baranovskii *et al.* [7] mentioned that Eq. (2) is valid only when μ and D are considered independent of energy, which is not the case for hopping transport or relaxation in an exponential band tail. Moreover, direct experimental evidence for the applicability of the generalized Einstein relation is poor. One of the most direct methods to probe the Einstein relation in organic semiconductors is by measuring the current density-voltage (J-V) characteristics of homojunction diodes in the diffusion-dominated regime, as shown by Harada *et al.* [11]. It was demonstrated that the (generalized) Einstein relation is directly represented in the common Shockley diode equation, which describes the J-V characteristics, given by [12]

$$J = J_0\left[\exp\left(\frac{qV}{gkT}\right) - 1\right], \tag{3}$$

with J_0 the saturation current density and g the enhancement factor of the classical Einstein relation [Eq. (2)]. It should be noted that the general diode equation is usually expressed as $J = J_0[\exp(qV/\eta kT) - 1]$, with η the ideality factor. The ideality factor can thus be regarded equal to the enhancement factor g in Eq. (2) and equals unity when the classical Einstein relation applies, under the condition that recombination is absent. In agreement with other studies [13,14], Harada *et al.* measured a temperature-dependent ideality factor, in accordance with the $g \propto 1/T$

dependence predicted by the generalized Einstein relation [10,15]. In this Letter, we measure the ideality factor for a large variety of organic semiconductor diodes, covering a wide range of energetic disorder. The ideality factors deviate from unity, suggesting an enhancement of the Einstein relation. However, this enhancement is temperature-independent and shows no relation to the amount of disorder, which strongly contradicts the concept of the generalized Einstein relation. We demonstrate that the classical Einstein relation in disordered semiconductors is valid when the nonequilibrium effects of deep charge traps are eliminated. This is achieved by using recombination as a means to release deeply trapped carriers.

In the present study, organic single-carrier diodes were prepared, where one electrode ensures Ohmic charge injection, while the counterelectrode blocks the injection of charges of opposite sign. The difference in work function of the electrodes gives rise to a built-in potential (V_{bi}) across the organic layer, causing a rectifying behavior. Typically, hole-only diodes were prepared on top of a glass substrate, patterned with a transparent indium-tin oxide electrode, on which a layer of conducting poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (Clevios CH8000) was spin-coated. Subsequently, a layer of organic semiconductor was spin-coated from solution under N_2 atmosphere. The devices were finished by thermal evaporation of an 80 nm Au cathode or an MoO_3(10 nm)/Al(100 nm) anode in some cases [16]. A variety of materials were tested, including regio-regular and regio-irregular poly(3-hexylthiophene) (rr- and rir-P3HT), poly(9,9-dioctylfluorene) (PFO), poly (triarylamine) (PTAA), PCPDTBT [17], and several poly(*p*-phenylene vinylene) (PPV) derivatives [18]. For the *n*-type fullerene derivatives PCBM and tbis-PCBM [19], electron-only diodes were prepared by evaporating a LiF/Al cathode. The electrical measurements were conducted under a controlled N_2 atmosphere, by using a Keithley 2400 source meter.

In Fig. 1, temperature-dependent *J*-*V* characteristics typical for single-carrier diodes are depicted. In these characteristics, three regimes can be distinguished. At low voltages, the weakly temperature-dependent leakage current (1) can be observed, caused by parasitical currents between the electrodes. In the second, diffusion-dominated regime, the current shows an exponential dependence on voltage according to Eq. (3) until V_{bi}. At V_{bi}, a transition to the space-charge limited drift regime (3) occurs [20], which is characterized by a quadratic dependence of the current on the voltage, according to the Mott-Gurney square law [21]. The slope of regime 2 is determined by the ideality factor η, which is conventionally deduced by fitting Eq. (3) to the experimental data. However, in order to prevent erroneous fitting, we determine the ideality factor by numerical differentiation according to

$$\eta = \left(\frac{kT}{q}\frac{\partial \ln J}{\partial V}\right)^{-1}. \quad (4)$$

By plotting this quantity against voltage, as shown in the inset in Fig. 1, the three regimes in the *J*-*V* characteristics can be distinguished again, where the ideality factor is obtained from the plateau value. The plateau value can be regarded as the steepest exponential incline of the *J*-*V* characteristics.

The temperature-resolved η-*V* characteristics of the PCBM electron-only diode in the inset in Fig. 1 show that the ideality factor, although slightly deviating from unity, is invariant over the whole temperature range. Such temperature-independent characteristics were observed for all investigated materials in this study. The observation of a temperature-independent ideality factor clearly contradicts the generalized Einstein relation, for which the disorder-induced enhancement scales inversely with temperature. In previous studies [11,13,14], ideality factors were found to increase with decreasing temperature. We found that this apparent increase of the ideality factor is an experimental artifact that is caused by a too large leakage current (regime 1). In that case, the leakage current masks the diffusion regime as the drift current reduces upon cooling, due to the temperature dependence of the mobility [22], and the plateau cannot be discerned anymore [23,24]. The apparent ideality factor will then be too high and temperature-dependent. Therefore, a reliable measurement of the ideality factor requires low leakage currents and high drift currents, enabling the observation of a clearly discernible exponential diffusion regime, as is the case in the measurement depicted in Fig. 1.

Another interesting feature appears when comparing the ideality factors of the investigated materials as a function of the room temperature carrier mobility, as depicted in Fig. 2. The ideality factor was determined from the temperature-independent plateau value of the differentiated

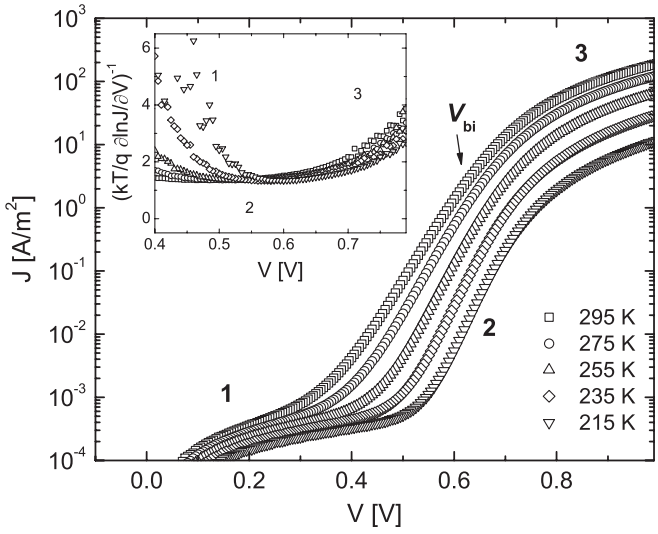

FIG. 1. Temperature-dependent *J*-*V* characteristics of a PCBM electron-only diode. The inset shows the differential plot of the data according to Eq. (4). The leakage (1), diffusion (2), and drift (3) regimes are indicated.

characteristics, and the room temperature zero-field mobility was determined by fitting the J-V characteristics in the drift regime with the well-known Mott-Gurney square law [21]. In a recent publication, Craciun, Wildeman, and Blom [22] have demonstrated that there is a universal relation between the mobility and its temperature activation. It is well established that the temperature dependence is a direct measure of the intrinsic disorder of the organic semiconductor [2,3]. As a result, the mobility can be regarded as a measure for the width of the DOS distribution. From Fig. 2, it appears that the value of the ideality factor is not related to intrinsic disorder of the semiconductor. In addition to the observed temperature independence, this again contradicts the generalized Einstein relation derived for a Gaussian DOS. The temperature independence of the ideality factor would be in agreement with the classical Einstein relation. However, the deviation from unity shows that the Einstein relation is disturbed. Nenashev *et al.* [8] recently demonstrated that the Einstein relation in disordered 3D hopping systems is violated even at small electric fields, which is mainly due to energetically deep, rare sites controlling the field dependence of the diffusivity. As the density of these sites is rather low, they do not affect the charge carrier mobility. Because of the long escape time from these deep states, deeply trapped carriers are not in thermal equilibrium with free carriers in the transport sites.

If deep trapping sites are the origin of the Einstein relation enhancement in single-carrier diodes, their effect would be obscured in double-carrier diodes, i.e., organic light-emitting diodes (OLEDs), where deep sites within the band gap act as recombination centers. Trapped charges will be released by free carriers of the opposite sign, neutralizing their effect on the transport. Recently, we reported that the ideality factor of an OLED generally has a value of 2, which originates from the presence of a dominant trap-assisted Shockley-Read-Hall (SRH) recombination mechanism in the diffusion regime [23]. Furthermore, free carrier recombination of the Langevin type was found to result in an ideality factor very close to unity. This was visualized in a white-emitting polymer, where red chromophores incorporated in the blue-emitting backbone function as emissive traps. Consequently, the red part of the emission arises from an SRH mechanism, whereas the blue emission is a result of Langevin recombination. The question is whether a disruption of the classical Einstein relation would still result in an SRH and Langevin ideality factor of 2 and 1, respectively. Therefore, device simulations were carried out by using a numerical drift-diffusion model [25], where the Einstein relation could be modified arbitrarily. It was observed that the introduction of an enhancement factor g simply modifies the SRH and Langevin ideality factors to $2g$ and $1g$, respectively. Figure 3 shows the luminance ideality factor for the red (SRH) part of the emission, which has a temperature-independent value of 2. As a result, the data can be described only by using the classical Einstein relation ($g = 1$). In addition, the η-V characteristics of the blue (Langevin) part of the emission (inset in Fig. 3) show excellent agreement with the simulations using the classical Einstein relation, complementing the results for the red emission. This confirms that the classical Einstein relation is valid ($g = 1$) and that deep trap states govern the enhancement in single-carrier diodes.

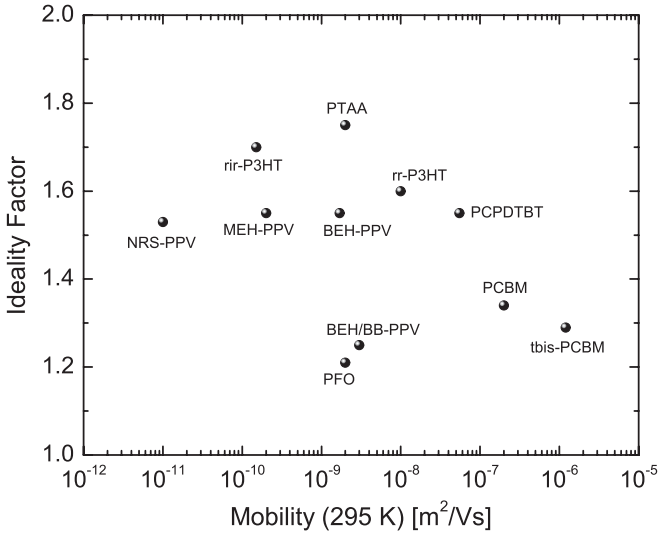

FIG. 2. The ideality factor of the investigated materials as a function of their zero-field mobility at 295 K, which can be regarded as a measure for the degree of disorder. This shows that the ideality factor and disorder are not related in these materials.

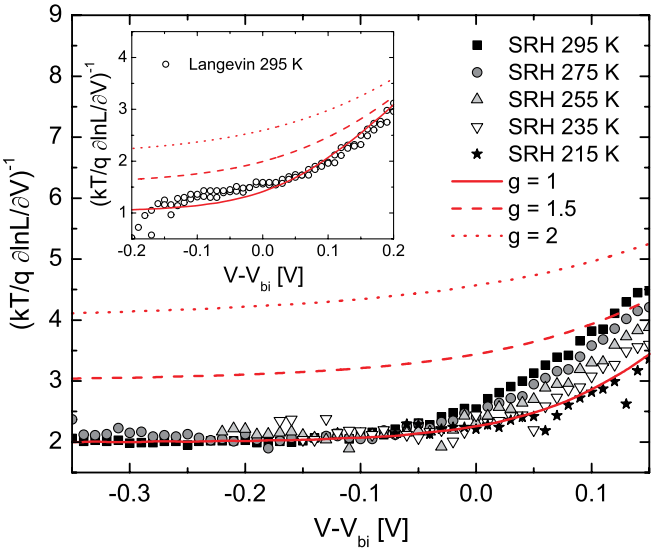

FIG. 3 (color online). Ideality factor derived from the luminance (L) for a 30 nm white OLED at different temperatures. A 550 nm long-pass filter was used to selectively transmit the red emission originating from SRH recombination. The inset shows the luminance ideality factor using a blue bandpass filter, measuring the blue emission originating from Langevin recombination. The lines represent the simulations from a drift-diffusion model using different values for the Einstein relation enhancement g.

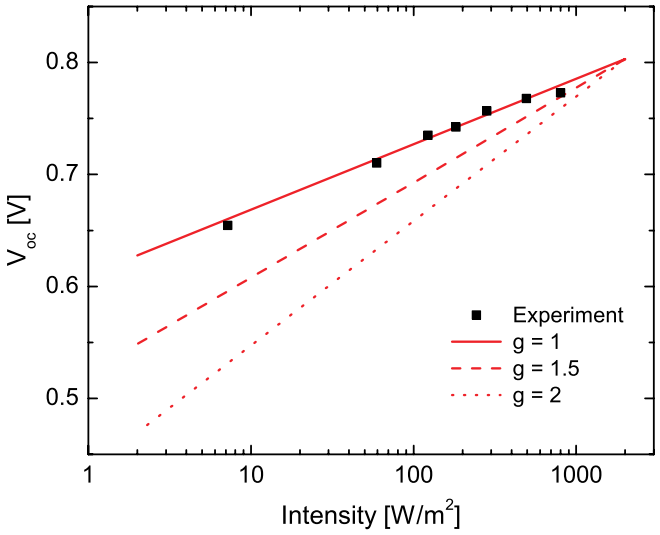

FIG. 4 (color online). V_{oc} vs light-intensity data (symbols) of a PPV:PCBM solar cell from Ref. [13]. The lines represent the simulations from a drift-diffusion model using different values for the Einstein relation enhancement g, normalized at $I = 2000$ W/m^2.

As a final step to confirm the validity of the classical Einstein relation, an organic solar cell has been considered. In organic solar cells, a blend of electron- and hole-transporting materials is used, where transport of both carriers can be regarded as virtually trap-free [25]. As a consequence, recombination in these devices arises predominantly from free charge carriers rather than trapped charge carriers. At the open-circuit voltage (V_{oc}) the current is zero, implying that recombination and photogeneration of charges cancel [26]. Since there is no net current, there exists a balance between drift and diffusion, creating an excellent environment to study the Einstein relation. Previous research [13] revealed a kT/q dependence of the V_{oc} on the logarithm of the incident light intensity (I). Equivalently to the case of the ideality factor, this dependence modifies to gkT/q when the Einstein relation is enhanced, as evidenced by simulations from the drift-diffusion model (Fig. 4). Hence, it is immediately obvious that a kT/q dependence of $V_{oc} - \ln(I)$ can be possible only when $g = 1$; i.e., the classical Einstein relation applies.

In conclusion, the validity of the Einstein relation in disordered organic semiconductors has been investigated by studying the diffusion-driven currents of single-carrier diodes. In contrast to earlier reports, a temperature-independent ideality factor was found for both n- and p-type conduction, which is in contradiction with the generalized Einstein relation derived for a Gaussian DOS. Furthermore, the ideality factor was observed to be irrelative of energetic disorder, and its deviation from unity was explained by the presence of energetically deep states within the band gap. The validity of the classical Einstein relation in disordered organic semiconductors was demonstrated in double-carrier devices as OLEDs and solar cells, where these traps are discharged by charge recombination.

The authors acknowledge the technical assistance of Jan Harkema and Frans van der Horst. The work of G. A. H. W. is supported by the Dutch Polymer Institute (DPI), Project No. 678. The work of L. J. A. K. is supported by a grant from STW/NWO (No. VENI 11166).

[1] A. Einstein, Ann. Phys. (Leipzig) **322**, 549 (1905).
[2] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[3] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, Phys. Rev. Lett. **81**, 4472 (1998).
[4] M. C. J. M. Vissenberg and M. Matters, Phys. Rev. B **57**, 12 964 (1998).
[5] R. Richert, L. Pautmeier, and H. Bässler, Phys. Rev. Lett. **63**, 547 (1989).
[6] P. M. Borsenberger, L. Pautmeier, R. Richert, and H. Bässler, J. Chem. Phys. **94**, 8276 (1991).
[7] S. D. Baranovskii, T. Faber, F. Hensel, P. Thomas, and G. J. Adriaenssens, J. Non-Cryst. Solids **198–200**, 214 (1996).
[8] A. V. Nenashev, F. Jansson, S. D. Baranovskii, R. Österbacka, A. V. Dvurechenskii, and F. Gebhard, Phys. Rev. B **81**, 115204 (2010), and references therein.
[9] D. Ritter, E. Zeldov, and K. Weiser, Phys. Rev. B **38**, 8296 (1988).
[10] Y. Roichman and N. Tessler, Appl. Phys. Lett. **80**, 1948 (2002).
[11] K. Harada, A. G. Werner, M. Pfeiffer, C. J. Bloom, C. M. Elliott, and K. Leo, Phys. Rev. Lett. **94**, 036601 (2005).
[12] W. Shockley, Bell Syst. Tech. J. **28**, 435 (1949).
[13] L. J. A. Koster, V. D. Mihailetchi, R. Ramaker, and P. W. M. Blom, Appl. Phys. Lett. **86**, 123509 (2005).
[14] K. Harada, M. Riede, K. Leo, O. R. Hild, and C. M. Elliott, Phys. Rev. B **77**, 195212 (2008).
[15] N. Tessler and Y. Roichman, Org. Electron. **6**, 200 (2005).
[16] H. T. Nicolai, G. A. H. Wetzelaer, M. Kuik, A. J. Kronemeijer, B. de Boer, and P. W. M. Blom, Appl. Phys. Lett. **96**, 172107 (2010).
[17] M. Lenes, M. Morana, C. J. Brabec, and P. W. M. Blom, Adv. Funct. Mater. **19**, 1106 (2009).
[18] C. Tanase, J. Wildeman, and P. W. M. Blom, Adv. Funct. Mater. **15**, 2011 (2005).
[19] R. K. M. Bouwer and J. C. Hummelen, Chem. Eur. J. **16**, 11 250 (2010).
[20] P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. **68**, 3308 (1996).
[21] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University, London, 1940).
[22] N. I. Craciun, J. Wildeman, and P. W. M. Blom, Phys. Rev. Lett. **100**, 056601 (2008).
[23] G. A. H. Wetzelaer, M. Kuik, H. T. Nicolai, and P. W. M. Blom, Phys. Rev. B **83**, 165204 (2011).
[24] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.107.066605 for details regarding the influence of leakage current.
[25] L. J. A. Koster, E. C. P. Smits, V. D. Mihailetchi, and P. W. M. Blom, Phys. Rev. B **72**, 085205 (2005).
[26] A. Maurano, R. Hamilton, C. G. Shuttle, A. M. Ballantyne, J. Nelson, B. O'Regan, W. Zhang, I. McCulloch, H. Azimi, M. Morana, C. J. Brabec, and J. R. Durrant, Adv. Mater. **22**, 4987 (2010).