IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

# The applicability of the transport-energy concept to various disordered materials

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 2699

(http://iopscience.iop.org/0953-8984/9/13/007)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.207
The article was downloaded on 14/05/2010 at 08:23

Please note that terms and conditions apply.

J. Phys.: Condens. Matter **9** (1997) 2699–2706. Printed in the UK PII: S0953-8984(97)77202-3

# The applicability of the transport-energy concept to various disordered materials

S D Baranovskii†, T Faber†, F Hensel† and P Thomas‡

† Fachbereich Physikalische Chemie und Zentrum für Materialwissenschaften der Philipps-Universität Marburg, D-35032 Marburg, Germany
‡ Fachbereich Physik und Zentrum für Materialwissenschaften der Philipps-Universität Marburg, D-35032 Marburg, Germany

Received 16 August 1996

**Abstract.** It is known that in disordered semiconductors with purely exponential energy distribution of localized band-tail states, as in amorphous semiconductors, all transport phenomena at low temperatures are determined by hopping of electrons in the vicinity of a particular energy level, called the transport energy. We analyse whether such a transport level exists also in materials with densities of localized states (DOSs) different from the purely exponential one. We consider two DOS functions $g(\epsilon) \sim \exp\{-(\epsilon/\epsilon_0)^\lambda\}$ with $\lambda = 2$, typical for polymers, heavily doped semiconductors, and, probably, liquid semiconductors and $\lambda = \frac{1}{2}$, typical for mixed crystals. It is shown that in both cases the transport energy exists, implying that it also exists for all intermediate forms of the DOS. Special attention is paid to the dependences of the transport level and of its width on the DOS parameters and temperature.

## 1. Introduction

In various disordered systems, such as liquid and amorphous semiconductors, doped crystalline materials, semiconductor alloys, and polymers, some electronic states at zero temperature are localized. If the Fermi level is located in the region of localized states the conductivity arises either from thermal excitation of carriers across a mobility gap into extended states or by hopping processes. The former mechanism must be inherent at high temperatures, while the latter one dominates electron transport at lower temperatures (Mott and Davis 1979, Enderby 1978). The borderline temperature which separates these two mechanisms depends on material parameters. Recently Fortner *et al* (1995) claimed that the hopping mechanism dominates the transport properties of various liquid semiconductors even at rather high temperatures ($T \sim 1000$ K), which makes the study of hopping transport especially interesting. While thermal activation of carriers into extended states can be easily interpreted theoretically (Overhof and Thomas 1989), hopping transport via localized band-tail states is rather difficult for a theoretical study, being crucially dependent on the density of localized states (DOS) (Shklovskii and Efros 1984). Computer simulations have mostly been used so far to study this mechanism. They provide some useful information on transport details, but do not allow a general description of the phenomenon.

Recently the very useful general concept of the so-called transport energy has been developed to describe hopping transport in band tails with purely exponential DOS. Such DOS can be described as

$$g(\epsilon) = (N_0/\epsilon_0)\exp(-\epsilon/\epsilon_0) \tag{1}$$

0953-8984/97/132699+08$19.50 © 1997 IOP Publishing Ltd 

where $\epsilon_0$ is the tailing parameter, $N_0$ is the total concentration of localized tail states, and the localization energy $\epsilon$ is measured positive from the mobility edge ($\epsilon = 0$) towards the gap centre. This shape of the DOS is widely assumed for amorphous materials.

The crucial role of a particular energy level in the hopping transport of electrons via localized band-tail states with the DOS of (1) was first recognized by Grünewald and Thomas (1979) and Grünewald *et al* (1979) in their analysis of equilibrium variable-range hopping conductivity. This problem was later considered by Shapiro and Adler (1985), who came to the same conclusion as Grünewald *et al*, i.e., that the vicinity of some particular energy level dominates the hopping transport of electrons in the band tail. In addition, they achieved an analytical formula for this level and showed that its position does not depend on the Fermi energy.

Independently, a rather different problem of non-equilibrium energy relaxation of electrons by hopping through the band tail with the DOS described by (1) was solved at the same time by Monroe (1985a, b). He showed that an electron, starting from the mobility edge, most likely makes a series of hops downward in energy. This character of the relaxation process changes at some particular energy $\epsilon_t$ which Monroe called the transport energy (TE). The hopping process near and below TE resembles dispersive transport, where $\epsilon_t$ plays the role of the mobility edge. The TE of Monroe (1985a, b) in the relaxation problem coincides exactly with the energy level discovered by Grünewald *et al* (1979) and Shapiro and Adler (1985) for equilibrium hopping transport.

Shklovskii *et al* (1990) have shown that the same energy level $\epsilon_t$ also determines both recombination and transport of electrons in the non-equilibrium steady state under continuous photogeneration in the exponential band tails.

We see, therefore, that in the DOS described by (1) this TE determines both equilibrium and non-equilibrium and both transient and steady-state transport phenomena. It was recently shown (Baranovskii *et al* 1995) why this energy level is so universal that hopping of electrons in its vicinity dominates various transport phenomena. It is the transport energy, which maximizes the hopping rate as a final electron energy in the hop between two localized states, independent of the initial energy.

All derivations of the TE so far have essentially been based on the purely exponential shape of the DOS. Such a DOS is widely accepted for amorphous semiconductors and the TE concept has proven to be very useful for describing various transport phenomena in such materials. The question arises of whether this concept can be generalized for a disordered system with a DOS different from that of (1). In fact, there are no consistent theoretical justifications of the purely exponential DOS in any disordered semiconductor. Moreover, in systems for which the DOS function can be calculated theoretically it differs from the purely exponential form of (1) (Zittartz and Langer 1966, Halperin and Lax 1966, 1967, Lifshitz *et al* 1982, Shklovskii and Efros 1984). The general situation with this DOS is the following. It is usually reasonable to assume that the distribution of the disordered potential which leads to the electron localization is Gaussian. This is the case for systems with rather different kinds of disorder. If this potential can be treated as a classical one, the distribution of localization energies reflects that of the potential and therefore can be described by a Gaussian function. This is often the case for, e.g., doped crystalline semiconductors (Shklovskii and Efros 1984) and organic polymers (Bässler 1993). Such a DOS has been also suggested for some fluid semiconductors (Popielawski *et al* 1979). A Gaussian DOS has the form

$$g(\epsilon) = (N_0/\pi^{1/2}\epsilon_0)\exp\{-(\epsilon/\epsilon_0)^2\} \qquad (2)$$

where notations are similar to those in (1), but the energy $\epsilon$ is measured just from the

distribution centre ($\epsilon = 0$), being positive towards deeper energies.

In other cases, the problem of electron localization must be treated quantum mechanically, i.e., it must be taken into account that the localization energy of electrons does not coincide with the depth of a potential well in which electrons are localized. In such a case the distribution function of electron energies (the DOS) differs from that of the localization potential and usually appears to be a weaker distribution function. This is known to be the case for crystalline semiconductor alloys (mixed crystals), where the DOS function is (Baranovskii and Efros 1978)

$$g(\epsilon) = (N_0/2\epsilon_0)\exp\{-(\epsilon/\epsilon_0)^{1/2}\} \tag{3}$$

with the same notations as in (1). It is even reasonable to suppose that DOS distributions for various disordered systems can be described by functions intermediate between those in (2) and (3). The challenging question then arises of whether one can extend the concept of TE, developed just for the DOS of (1), to systems with DOS functions described by (2) and (3).

This question was recently addressed by Hartenstein and Bässler (1995) for the case of a Gaussian DOS. The authors used computer simulation and concluded that the results of the simulations were obscured by oscillation transitions of electrons between energetically close sites. It is difficult, therefore, to find from their results whether or not the transport level exists for the chosen DOS of (2).

Below we solve this problem analytically for the two DOS functions described by (2) and (3). In section 2, a general formalism is given for the derivation of the TE. In sections 3 and 4 we apply it to the DOS functions described by (2) and (3) respectively. It will be shown that the TE exists in both cases, implying that it exists also for DOS functions intermediate between those described by (2) and (3). Of course, the transport level depends strongly on the DOS parameters. Concluding remarks are gathered in section 5.

## 2. Derivation of the transport energy in a hopping system

In our derivation we assume the simplest form for the hopping rates of electrons between localized states

$$\nu_{ij} = \nu_0 \exp(-2R_{ij}/\alpha - (\epsilon_i - \epsilon_j + |\epsilon_j - \epsilon_i|)/2kT). \tag{4}$$

Here $\nu_{ij}$ is the rate for the hop between an occupied site $i$ and an empty site $j$ separated by distance $R_{ij}$; $\alpha$ is the decay length of the wave function of the tail states; $\nu_0$ is the attempt-to-escape frequency.

Let us consider an electron in a tail state at energy $\epsilon_i$. The median rate of a downward hop of such an electron to a neighbouring localized state with some energy $\epsilon_j \geqslant \epsilon_i$ is

$$\nu \downarrow (\epsilon_i) = \nu_0 \exp(-2R(\epsilon_i)/\alpha) \tag{5}$$

where

$$R(\epsilon_i) \simeq \left\{(4\pi/3)_\epsilon \int_i^\infty g(x)\,\mathrm{d}x\right\}^{-1/3}. \tag{6}$$

The median rate of an upward hop of such an electron to a neighbouring localized state with energy $\epsilon_j \leqslant \epsilon_i$ is

$$\nu_\uparrow(\epsilon_i, \delta) = \nu_0 \exp(-2R(\epsilon_i - \delta)/\alpha - \delta/kT) \tag{7}$$

where $\delta = \epsilon_i - \epsilon_j \geqslant 0$. This expression is not exact, of course. The average nearest-neighbour distance $R$ used is based on all states deeper than $\epsilon_i - \delta$. For an exponential

tail this is equivalent to considering a slice of energy of width $\epsilon_0$. This works well for a distribution that varies slowly compared to $kT$, but not in general. A more correct and sophisticated description allows a competition between all states appropriately weighted with a Boltzmann factor for upward hops (Monroe 1985b, Stoddart *et al* 1988). For the shapes of the DOS considered here, this differs from the current derivation by factors of order unity in the logarithm (Baranovskii *et al* 1995). Therefore we use the foregoing formulation of hopping rates for simplicity and clarity.

We will analyse these hopping rates at a given temperature $T$ and try to find the energy difference $\delta$ which provides a fastest typical hopping rate for an electron placed initially at energy $\epsilon_i$. The corresponding energy difference $\delta$ is determined by the condition

$$\partial \nu_{\uparrow}(\epsilon_i, \delta)/\partial \delta = 0. \tag{8}$$

For the purely exponential DOS, using (1) and (6)–(8), we find that the hopping rate in (7) has its maximum at

$$\delta = \epsilon_i - 3\epsilon_0 \ln[3\epsilon_0 (4\pi N_0/3)^{1/3} \alpha/2kT]. \tag{9}$$

The second term in the right-hand side of (9) is called the transport energy $\epsilon_t$ after Monroe (1985a, b)

$$\epsilon_t = 3\epsilon_0 \ln[3\epsilon_0 (4\pi N_0/3)^{1/3} \alpha/2kT]. \tag{10}$$

The fastest hop occurs to the state in the vicinity of the transport energy $\epsilon_t$, independent of the initial energy $\epsilon_i$, provided $\epsilon_i$ is deeper in the tail than $\epsilon_t$, i.e. if $\delta \geqslant 0$. This coincides with the previous results of Monroe (1985a, b) and Kemp and Silver (1991). The width $W$ of the maximum of the hopping rate is determined by the requirement that near $\epsilon_t$ the hopping rate $\nu_{\uparrow}(\epsilon_i, \delta)$ differs by less than a factor of $e$ from the value $\nu_{\uparrow}(\epsilon_i, \epsilon_i - \epsilon_t)$. One finds (Shklovskii *et al* 1990)

$$W = (6\epsilon_0 kT)^{1/2}. \tag{11}$$

For states with $\epsilon_i \leqslant \epsilon_t$, the fastest hop is a downward hop to a nearest neighbour at some energy $\epsilon \geqslant \epsilon_i$ with the rate described by (5) and (6). This means that electrons in the shallow states with $\epsilon_i < \epsilon_t$ hop normally into deeper states with $\epsilon > \epsilon_i$, whereas electrons in the states with $\epsilon_i > \epsilon_t$ hop usually to states near $\epsilon_t$ in the energy interval $W$ determined by (11). This result implies that $\epsilon_t$ must play a crucial role in those phenomena which are determined by hopping of electrons in band tails.

## 3. Transport energy in a Gaussian DOS

A Gaussian-shaped DOS is usually assumed for random organic solids such as polymers (Bässler 1993) and is known to be valid for most cases in doped crystalline materials (Shklovskii and Efros 1984). Recently it was claimed that replacement of the exponential DOS by a Gaussian one precludes an analytic solution of the TE problem, and a Monte Carlo computer simulation was carried out, which brought, however, a rather obscure result (Hartenstein and Bässler 1995). Indeed, for a Gaussian DOS it is not possible to carry out an analytic derivation of the TE described in section 1 up to the final result. We show below however that it is possible to derive analytically an equation for the transport energy in a Gaussian DOS, which can be solved numerically. This method requires a computer just for the numerical solution of the derived equation and not for a Monte Carlo simulation.

Substituting (2) into (6)–(8) one obtains the following expression for the quantity $x = (\epsilon_i - \delta)/\epsilon_0$:

$$e^{x^2}\left(\int_x^\infty e^{-t^2}dt\right)^{4/3} = \frac{2}{3}\left(\frac{4\pi}{3}N_0\alpha^3\right)^{-1/3}\pi^{1/6}\frac{kT}{\epsilon_0}. \qquad (12)$$

It is noteworthy that the very structure of this equation implies the existence of the transport energy for the Gaussian DOS. Indeed, if we denote the solution of (12) as $x = x_0(T, N_0, \alpha, \epsilon_0)$, then the quantity

$$\epsilon_t = \epsilon_0 x_0(T, N_0, \alpha, \epsilon_0) \qquad (13)$$

is the transport energy, according to its definition in section 1. It is clear from (12) that the value of $\epsilon_t$ depends only on two parameters $N_0\alpha^3$ and $kT/\epsilon_0$.

The transport energy $\epsilon_t$ maximizes the hopping rate as a final electron energy in a hop between two localized states independent of the initial energy. The sharpness of this maximum determines the width of the transport path. Mathematically this width is determined by the requirement that near $\epsilon_t$ the hopping rate $\nu_\uparrow(\epsilon, \delta)$ differs by less than a factor of e from the value $\nu_\uparrow(\epsilon, \epsilon - \epsilon_t)$. After solving (12) we have put the solution into (7) and found the width $W$ of the transport path according to the above definition. The results of the numerical solution of (12) are shown in figure 1 along with the width $W$. The energy in figure 1 is measured positive downward from the centre of the distribution ($\epsilon = 0$). In figure 1(a) results are shown for $N_0\alpha^3 = 0.02$, which is the upper limit of $N_0\alpha^3$ for the absence of the extended states in the DOS distribution (Shklovskii and Efros 1984). The transport level $\epsilon_t$ is located in the lower part of the DOS at almost all temperatures $kT < \epsilon_0$. The width $W$ of the transport level remains small ($W < \epsilon_0$) up to $kT \approx 0.4\epsilon_0$. With decreasing concentration of states in the band tail, i.e., decreasing parameter $N_0\alpha^3$, the transport energy $\epsilon_t$ shifts at higher temperatures to the upper half of the DOS distribution (i.e., becomes negative) as is clearly seen in figure 1(b) for $N_0\alpha^3 = 0.001$. This occurs because at low concentrations $N_0$ it is favourable for electrons to be activated to higher energies, increasing the concentration of available hopping sites. This reflects the very nature of the TE and of the variable-range-hopping processes in general.

The results in figure 1 show that the concept of TE provides a good approximation for the description variable-range hopping in a Gaussian DOS at thermal energies smaller than the tailing parameter $\epsilon_0$, i.e., in the case in which transport is via hopping in the band tails.

## 4. Transport energy for DOS $g(\epsilon) \sim \exp\{-(\epsilon/\epsilon_0)^{1/2}\}$

Recent advances in epitaxial crystal growth techniques allow the fabrication of a variety of optoelectronic and microwave devices having a semiconductor alloy (a mixed crystal) as an important constituent. Because of the randomness in the distribution of the alloy components in the crystalline lattice, mixed crystals possess pronounced band tails near the mobility edges. The DOS distribution in such tails caused by Gaussian spatial fluctuations is described by (3) (Baranovskii and Efros 1978). It is, of course, of high interest to analyse hopping transport in such a system. In the following we check whether the concept of transport energy is applicable in this case.

Substituting (3) into (6)–(8) one obtains the following expression for the quantity $x = (\epsilon_i - \delta)/\epsilon_0$:

$$\ln\{(3\epsilon_0/kT)(4\pi N_0\alpha^3/3)^{1/3}\} = x^{1/2}/3 - \tfrac{4}{3}\ln\{1 + x^{1/2}\}. \qquad (14)$$

The structure of this equation implies the existence of the TE. Indeed, if $x_0(kT/\epsilon_0, N_0\alpha^3)$ is the solution of (14), the quantity $\epsilon_t$ determined by (13) is the transport energy.

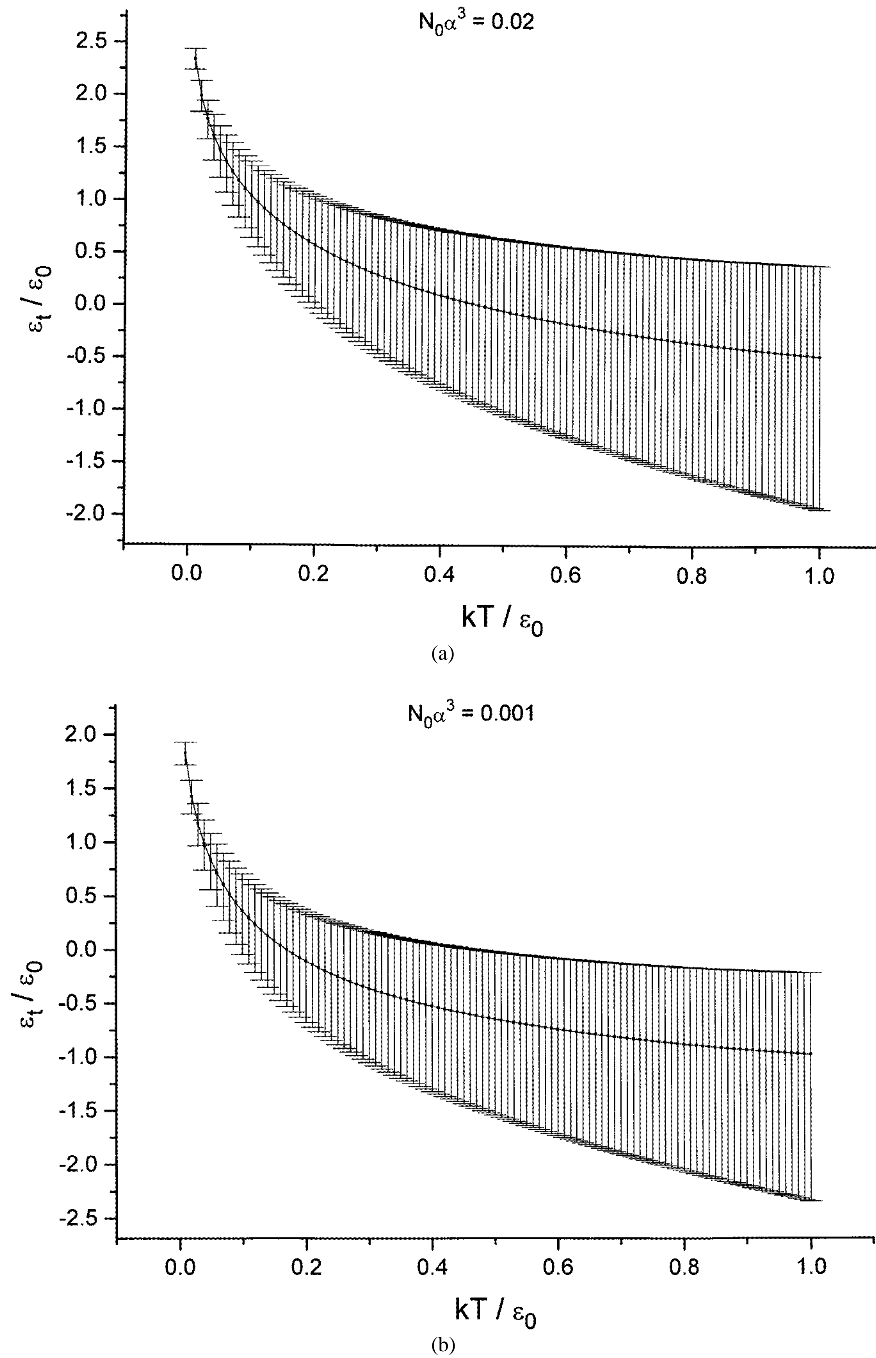
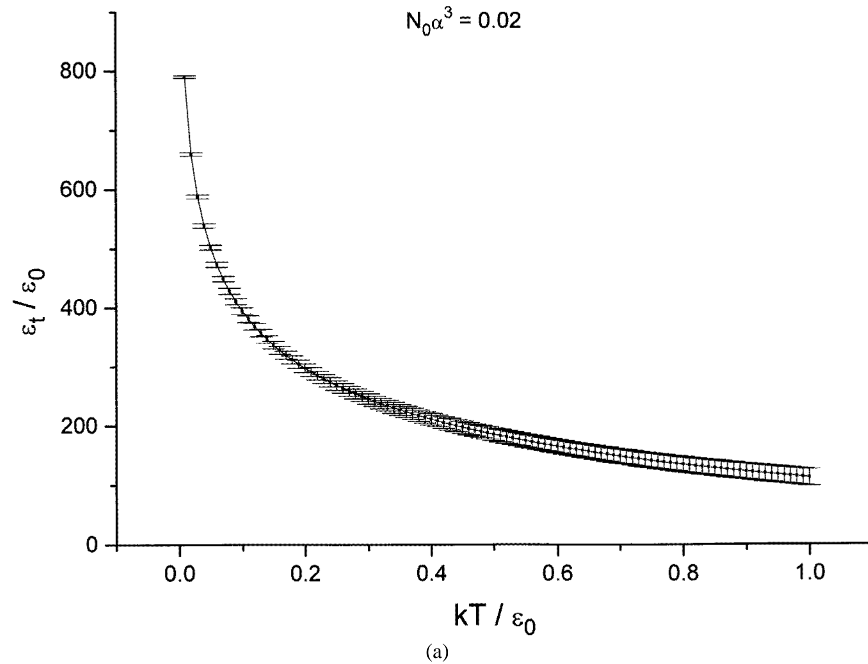
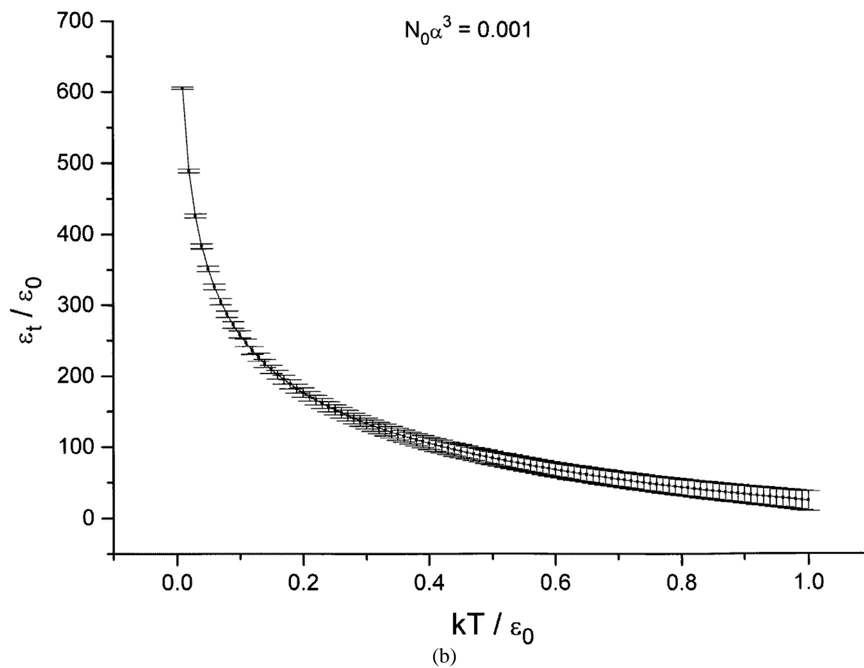



**Figure 1.** Temperature dependences of the transport energy $\epsilon_t$ and its width (shown by vertical lines) for a Gaussian DOS: (a) $N_0\alpha^3 = 0.02$; (b) $N_0\alpha^3 = 0.001$.

In figure 2 solutions for $\epsilon_t$ are shown along with the width $W$ of the transport level analogous to those shown in figure 1 for a Gaussian tail. Energy $\epsilon$ in figure 2 is measured positive from the mobility edge towards the gap centre, as in (3). It is clearly seen that




(a)




(b)

**Figure 2.** Temperature dependences of the transport energy $\epsilon_t$ and its width (shown by vertical lines) for the DOS of (3): (a) $N_0\alpha^3 = 0.02$; (b) $N_0\alpha^3 = 0.001$.

formally the transport energy exists in the DOS of (3). However it is located extremely deep in the tail ($\epsilon_t \gg \epsilon_0$) for temperatures of interest $kT < \epsilon_0$ at which transport is via hopping in the band tails. According to the derivation of the transport energy $\epsilon_t$, electrons

in the shallow states with $\epsilon < \epsilon_t$ make hops downward in energy to a nearest neighbour with the energy deeper than $\epsilon$. Such energy-loss hopping is not influenced significantly by temperature and can be well described by a simple model (Shklovskii *et al* 1989). Our result that $\epsilon_t$ is located very deep in the tail justifies the application of this simple approach to the hopping in the DOS of (3) in a very broad temperature range $kT < \epsilon_0$.

## 5. Conclusions

It is shown that the concept of TE provides a useful tool to describe transport processes not only in systems with purely exponential DOS (e.g., amorphous semiconductors), but also in systems with a Gaussian DOS (e.g., polymers) and in systems with the DOS of (3) (e.g., semiconductor alloys), thus implying that it is also valid for systems with a DOS intermediate between those of (2) and (3). This result is obtained analytically and it does not suffer from complications found in recent Monte Carlo computer simulations.

While for a Gaussian DOS the transport energy is located in the central part of the DOS distribution at DOS parameters and temperatures relevant to those in experimental studies, the position of the TE for the DOS of (3) appears to be extremely deep in the tail, implying that the simplest energy-loss hopping model is a good description of transport properties in systems with such a DOS.

## Acknowledgment

Financial support by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 383 is gratefully acknowledged.

## References

Baranovskii S D and Efros A L 1978 *Sov. Phys.–Semicond.* **12** 1328
Baranovskii S D, Thomas P and Adriaenssens G J 1995 *J. Non.-Cryst. Solids* **190** 283
Bässler H 1993 *Phys. Status Solidi* b **175** 15
Enderby J E 1978 *The Metal Non-Metal Transition in Disordered Systems (Scottish Universities Summer School in Physics; St Andrews, August 1978)* ed L R Friedman and D P Tunstall (Edinburgh: SUSSP Publication) p 425
Fortner J, Karpov V G and Saboungi M-L 1995 *Appl. Phys. Lett.* **66** 997
Grünewald M and Thomas P 1979 *Phys. Status Solidi* b **94** 125
Grünewald M, Thomas P and Würtz D 1979 *Phys. Status Solidi* b **94** K1
Halperin B I and Lax M 1966 *Phys. Rev.* **148** 722
——1967 *Phys. Rev.* **153** 802
Hartenstein B and Bässler H 1995 *J. Non-Cryst. Solids* **190** 112
Kemp M and Silver M 1991 *Phil. Mag.* B **63** 437
Lifshitz I M, Gredeskul S A and Pastur L A 1982 *Introduction to the Theory of Disordered Systems* (Moscow: Nauka)
Monroe D 1985a *Phys. Rev. Lett.* **54** 146
——1985b *PhD Thesis* Massachusetts Institute of Technology
Mott N F and Davis E A 1979 *Electronic Processes in Non-Crystalline Materials* (Oxford: Clarendon)
Overhof H and Thomas P 1989 *Electronic Transport in Hydrogenated Amorphous Semiconductors* (Berlin: Springer)
Popielawski J, Uchtmann H and Hensel F 1979 *Ber. Bunsenges. Phys. Chem.* **83** 123
Shapiro F R and Adler D 1985 *J. Non-Cryst. Solids* **74** 189
Shklovskii B I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (Heidelberg: Springer)
Shklovskii B I, Fritzsche H and Baranovskii S D 1989 *Phys. Rev. Lett.* **62** 2989
Shklovskii B I, Levin E I, Fritzche H and Baranovskii S D 1990 *Advances in Disordered Semiconductors* vol 3, ed H Fritzsche (Singapore: World Scientific) p 161
Stoddart H A, Vardeny Z and Tauc J 1988 *Phys. Rev.* B **38** 1362
Zittartz J and Langer J S 1966 *Phys. Rev.* **148** 741