Nonexponential relaxation dynamics of localized carrier densities in oxide crystals without structural or energetic disorder

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A microscopic model for the nonexponential relaxation of localized-charge carrier densities in oxide crystals is derived by taking into account thermally activated diffusive hopping transport and the effect of trap saturation. Thereby it is shown that the relaxation, commonly described by a stretched-exponential function, can be successfully reconstructed without consideration of a structural or energetic disorder. Furthermore, the access to particular microscopic measures such as the lifetime of single hopping events and localized-carrier densities is enabled. The impact of the model approach valid for various complex relaxation processes is demonstrated with the nonexponential relaxation dynamics of optically generated small bound polaron densities experimentally determined in $KNbO_3$ as an example.

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I. INTRODUCTION

Nonexponential relaxations are often encountered in solid-state physics.[1–3] Examples for this effect are temporal decays of the densities of photoexcited electrons and holes, bound to shallow defects (small polarons).[4–9] In recent years these decay shapes have often been deliberately described by stretched-exponential functions according to the empirical dielectric decay function by Kohlrausch, Williams, and Watts (KWW):[10]

$$f_{\mathrm{KWW}}(t) = f_0 \exp\left[-(t/\tau_{\mathrm{KWW}})^{\beta}\right], \tag{1}$$

with the initial amplitude f_0, mean lifetime τ_{KWW}, and stretching exponent $0 < \beta \leqslant 1$. Although Eq. (1) is at first a macroscopic phenomenological description, it has nonetheless been rather successful in fitting the decay shapes of the above-named relaxations.[5–9] However, in most cases a derivation of Eq. (1) from basic microscopic theoretical models concerning the specific problem under study remained unsatisfactory. Among the most promising explanations are those employing structural and/or energetic disorder of the crystal lattice, or direct hopping transitions to spatially distant sites.[2,5,6,11] A severe drawback is that important microscopic parameters, such as carrier and trap densities, and transition lifetimes, are not inherent to these theories.

In this Brief Report we present a microscopic theory for the thermally activated diffusive transport of excited charge carriers via nearest-neighbor hopping transitions. For this type of transport, a mathematical description is derived, based on the theory of random walks according to Pólya.[12,13] It will be shown that even in a perfect crystal without further energetic disorder, one will end up with a strongly nonexponential relaxation, given that one physical effect is allowed: trap saturation. This notion describes the simple fact that a trap (e.g., an acceptor-type defect) is neutralized once a free-charge carrier has recombined with it. This causes a depletion of both immobile traps and free carriers with proceeding time. This trap-saturation effect (TSE) is basically independent of dimensionality and crystal symmetry; we will treat the problem here exemplarily for a three-dimensional simple cubic lattice, which resembles the above-mentioned physical systems. For the important case where the number of free carriers equals that of the traps, the temporal development can be well described by a bimolecular reaction.[4] Our mathematical approach is applied to the results of numeric random-walk transport simulations, as well as to the decay of light-induced absorption changes, with the oxide $KNbO_3$ as an example. In comparison to earlier attempts,[4,14] we highlight the possibility to determine the values for the lifetime of a single hopping event and the density of the excited carriers from the experimentally obtained relaxation shape.

II. MICROSCOPIC MODEL

We will first derive the relevant formulas describing the temporal development of the density of charge carriers (i.e., walkers in the random-walk formalism). We assume an initial relative density $q[0]$ of randomly placed point defects (traps). Here $q = N_{\mathrm{traps}}/N_{\mathrm{sites}} < 1$, that is, the number density of traps divided by the number density of possible sites, making q a dimensionless quantity. Excited charge carriers of density $\nu[0] = q[0]$ are injected into the spatially infinite lattice at randomly chosen nontrapping sites at time zero. From there they diffuse solely by thermally activated hopping until they encounter a trap, where recombination occurs, and both carrier and trap are removed from the lattice. It is assumed that the carriers are not influenced by external or internal electromagnetic driving forces, e.g., space-charge fields or electron-hole interactions. That means, the walk is unbiased, fulfilling the conditions for a *homogeneous lattice walk*.[13] The distribution of lifetimes for a single step of the walk is assumed to be monoexponential with mean lifetime τ_0, according to the probability density function

$$\psi[t] = \tau_0^{-1} \exp\left[-t/\tau_0\right]. \tag{2}$$

Thus the mean lifetime for n successive steps is $n\tau_0$. Since a random walker may only be trapped upon first passage of

a given site, we introduce the probability Δ_n to visit such a "virgin" site on the nth step of the walk. Then the probability to survive *at least* n steps is

$$p_S[n] = \prod_{i=1}^{n}(1 - \Delta_i q[i]), \tag{3}$$

where $q[i]$ denotes the relative trap density at step number i. Since by definition $q[n] \equiv \nu[n]$, the walker density is given as

$$\nu[n] = \nu[0]p_S[n], \tag{4}$$

which is equivalent to the recurrence equation

$$\nu[n] = \frac{\nu[n-1]}{1 + \Delta_n \nu[n-1]}. \tag{5}$$

The solution of Eq. (5) is

$$\nu[n] = \frac{\nu[0]}{1 + \nu[0]\sum_{i=1}^{n}\Delta_i}. \tag{6}$$

The above-given formulas are independent of both lattice type and dimensionality (they are in fact valid for homogeneous random walks in general).[13] As Montroll and Weiss have found,[15] for a homogeneous lattice walk the variable Δ_n depends on the first-passage probabilities $F_n(\mathbf{s})$, accumulated over all possible lattice sites $\mathbf{s}$:

$$\Delta_n = -F_n(\mathbf{0}) + \sum_{\mathbf{s}} F_n(\mathbf{s}). \tag{7}$$

Elimination of $F_n(\mathbf{s})$ by the occupation probability $P_n(\mathbf{s})$ leads to the simplified relation[13]

$$\Delta_n = 1 - P_n(\mathbf{0}) - \sum_{i=1}^{n-1} P_{n-i}(\mathbf{0})\Delta_i, \tag{8}$$

where the vector $\mathbf{0}$ denotes the spatial origin of the walk. All relevant information about the specific lattice is contained in the value $P_n(\mathbf{0})$. In the present case of a three-dimensional simple cubic lattice, $P_n(\mathbf{0}) = 0$, if n is odd, otherwise

$$P_n(\mathbf{0}) = \frac{16\,\Gamma[n]^2}{6^n n^2 \Gamma\left[\frac{n}{2}\right]^4} \sum_{k=0}^{\infty} \frac{\left(-\frac{n}{2}\right)_k \left(-\frac{n}{2}\right)_k \left(-\frac{n}{2}\right)_k}{\left(-\frac{n-1}{2}\right)_k (1)_k 4^k k!}, \tag{9}$$

where $(a)_k$ is the Pochhammer symbol.[13] The validity of Eq. (9) was checked by direct enumeration of all possible walks up to $n = 11$. The virgin-site probability and its cumulative sum as a function of the step number, calculated from Eq. (8), are shown in Fig. 1.

Having established a formula for the walker density in terms of step numbers, we may now ask for its applicability to a physical observable. Our example will be transient absorption due to optically induced metastable small electron and hole polarons in $KNbO_3$ (*light-induced absorption*). Here, the *bound* hole polarons represent traps and the *free* electron polarons act as walkers.[16] Thus, we have to relate the step-number-dependent dimensionless walker density $\nu[n]$ to the time-dependent light-induced absorption $\alpha_{li}[t]$. This transformation is done by first approximating n by t/τ_0 [see Eq. (2)]. For the second simplification we note that for sufficiently long walks, $\sum_{i=1}^{n}\Delta_i$ grows almost linearly with the number of steps taken, as can be seen from Fig. 1. We can therefore replace the sum in Eq. (6) by the linear term

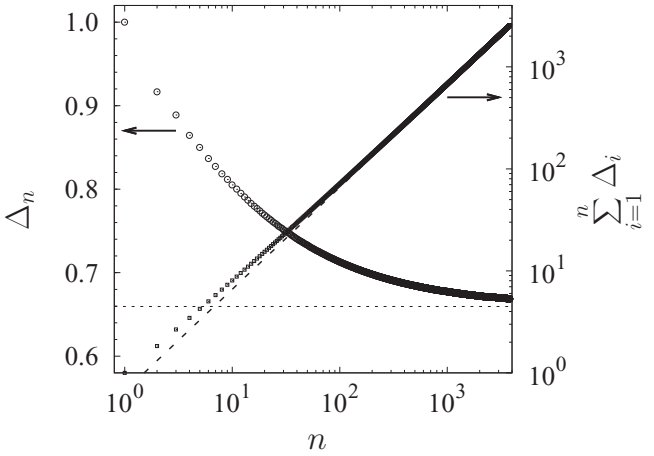

FIG. 1. Virgin-site probability Δ_n as a function of the number of steps taken. The right-hand plot shows the sum of Δ_i over n according to Eq. (8). The dashed lines mark the asymptotic limits $1 - R \approx 0.659\,463$ and $(1 - R)n$, respectively.

$(1 - R)n$, where R denotes the probability of eventual return to the initial site.[12,13,15] One finds that Eq. (6) takes the form

$$\nu[t] = \left(\frac{1}{\nu[0]} + \frac{1-R}{\tau_0}t\right)^{-1}, \tag{10}$$

which is the solution to the bimolecular reaction equation

$$\frac{d}{dt}\nu[t] = -\frac{1-R}{\tau_0}\nu[t]^2. \tag{11}$$

Light-induced absorption is connected to the number density of absorption centers (i.e., the walker density) $\alpha_{li} = \sigma N_{sites}\nu$, where σ denotes the joint absorption cross section of the electron and hole polarons.[16,17] Combining these relations, we find a formula for the decay of the light-induced absorption, according to our model:

$$\alpha_{li}[t] = \left(\frac{1}{\alpha_{li}[0]} + \frac{1-R}{\sigma N_{sites}\tau_0}t\right)^{-1}. \tag{12}$$

Hence, we established a connection between the macroscopic observable $\alpha_{li}[t]$ and the microscopic quantities τ_0, σ, and $\nu[t]$.

III. SIMULATIONAL AND EXPERIMENTAL DETAILS

The simulation proceeds on a $100 \times 100 \times 100$ site simple cubic supercell with periodic boundary conditions, containing an initial density of randomly placed traps and excited carriers. It is essential that all carriers perform their walks simultaneously in order to properly mimic the situation in real materials. In our case the trap and walker densities are chosen to be $q[0] \approx \nu[0] \approx 10^{-3}$, so that each carrier's history is sufficiently long. The mean lifetime for single hopping events τ_0 is set to unity. It is obvious that the duration of walks increases with decreasing trap (walker) density. To achieve finite computation times, we choose a walker density slightly less than the trap density: $\nu[0]/q[0] = 0.99$. In order to have sufficient statistics, the supercell is reinitialized after all walkers have recombined, starting a new diffusive process. In total, between 10^5 and 10^6 individual carrier histories are

recorded and averaged. Simulations without the TSE result in simple exponential decay shapes.

Measurements of the light-induced absorption were conducted in undoped $KNbO_3$ using a pump-probe setup described in Refs. 8, 9, and 16. The data shown here are taken from Torbrügge *et al.*[16]

IV. RESULTS AND DISCUSSION

Figure 2(a) shows the temporal development of the walker density for a ratio of walkers and traps of $\nu[0]/q[0] = 0.99$. In Fig. 2(b) the experimental data for the decay of $\alpha_{\rm li}[t]$ in $KNbO_3$ are shown. Both data sets are analyzed using the KWW function [Eq. (1)] and the functions derived from our microscopic theory, taking TSE into account [Eqs. (10) and (12)]. The respective fit parameters are summarized in Table I. In the case of $KNbO_3$, the following assumptions entered the TSE model approach: $1 - R = 0.659\,463$,[13] $\sigma = 6 \times 10^{-22}$ m^2,[17] and $N_{\rm sites} = 1.55 \times 10^{28}$ m^{-3}.[18] As can be seen, in either case the TSE model fits the data in an excellent way through at least five orders of magnitude of process time. It resembles the decay shape even better than the KWW model of our earlier analyses.[8,9,16] This observation is further emphasized by subtracting the fits from the experimental (simulational) data, as shown in the lower parts of Figs. 2(a) and 2(b). In both cases, the overall difference between data and fit is much smaller for the TSE model as compared to the KWW fit. The latter shows characteristic positive deviations for short and long times, and a dip in the region of $\tau_{\rm KWW}$.

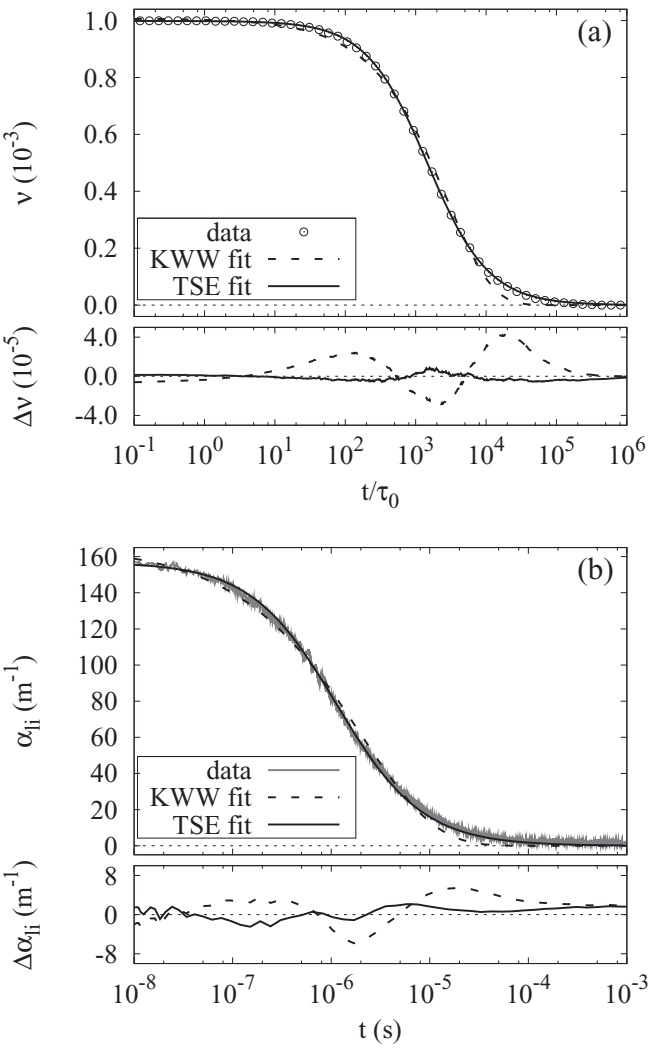

FIG. 2. (a) Temporal development of the walker density (open circles) for a walker and trap ratio of $\nu[0]/q[0] = 0.99$. (b) Decay of the light-induced absorption in undoped $KNbO_3$ at $\lambda = 785$ nm (gray line). The dashed and solid black lines are fits according to the KWW [Eq. (1)] and the TSE model [Eqs. (10) and (12)], respectively. The fit parameters are summarized in Table I. In order to illustrate the fit quality, difference plots are given below the respective principal data plots. In the case of $KNbO_3$, these plots have been smoothed to enhance the visibility.

TABLE I. Fit parameters as taken from fits of Eq. (1) (upper part) and Eqs. (10) and (12) (lower part) to the data of Fig. 2. For details concerning the calculation of $\nu[0]$ and τ_0 in the TSE model, see the text.

KWW	$\alpha_{\rm li}[0]$ (m^{-1})	$\tau_{\rm KWW}$ (s)	β
Simul.	0.0010 ± 0.0001	2800 ± 200	0.68 ± 0.08
$KNbO_3$	166 ± 10	$(2.0 \pm 0.8) \times 10^{-6}$	0.58 ± 0.05
TSE	$\alpha_{\rm li}[0]$ (m^{-1})	τ_0 (s)	$\nu[0]$ (10^{-5})
Simul.	–	0.98 ± 0.04	99 ± 1
$KNbO_3$	157 ± 2	$(1.3 \pm 0.8) \times 10^{-11}$	1.7 ± 0.8

In the following we want to discuss the applicability of our theory as well as possible relations to the KWW model.

Probably the most remarkable feature of the TSE model is its ability to yield the lifetime of one single hopping event. For the thermally activated transport of small polarons one finds the relation[19]

$$\tau_0^{-1} \approx m \frac{J^2}{\hbar} \sqrt{\frac{\pi}{4 E_{\rm a} k_{\rm B} T}} \exp\left[-\frac{E_{\rm a}}{k_{\rm B} T}\right]. \qquad (13)$$

Taking into account the experimental values $\tau_0 \approx 1.3 \times 10^{-11}$ s and $E_{\rm a} = 0.14$ eV,[16,20] and assuming for the number of nearest neighbors $m = 6$, one finds for the polaronic bandwidth $J \approx 0.01$ eV, which implies a nonadiabatic hopping process.

Assumptions have to be made about the parameters R, σ, and $N_{\rm sites}$, whose values are usually known with high accuracy. The site density $N_{\rm sites}$ is easily obtained from crystallographic and chemical data, and σ can be estimated—if not already known—from similar systems, such as $LiNbO_3$.[17] For many color centers $\sigma \approx (5\text{–}15) \times 10^{-22}$ m^2 is a reasonable value. Finally, the structure parameter R does not vary significantly for different three-dimensional lattices:[13] $0 < R < 0.5$. Thus, the relative error for the derived parameters τ_0 and ν will be of the order of unity.

Despite this high accuracy, there are certain limits to the theory. Perhaps the most important one is that the approximations used are only valid for large step numbers n, as can be seen in Fig. 1. Therefore, since $n \approx q[0]^{-1}$, relatively small trap and walker densities are a prerequisite: We estimate $q[0] \lessapprox 0.01$ as a reasonable value. Interestingly, a similar value ($q[0] < 0.001$) has been stated as mandatory for stretched-exponential relaxation to occur in a simple cubic system.[14]

Figure 1 shows that this value is close to the asymptotic limit, effectively used in our analytic approximation. However, in most polar oxides, e.g., $KNbO_3$, and more so for common semiconductors, this requirement is fulfilled to a great extent. We further note that even for short time values, representing short walks, the TSE model still fits the data well, although the above-mentioned requirements are not strictly fulfilled.

Concerning possible relations between the KWW and TSE models, we note the following. Given the prerequisites of the microscopic approach to the charge transport are fulfilled, the TSE model will yield meaningful results for the microscopic measures τ_0 and ν. The KWW model in turn, while it may be applied to a large class of decays, gives only vague hints about the underlying mechanisms, e.g., activation energies.

From a rigorous point of view, a direct comparison between the two models seems inadequate as they represent different mathematical objects. This is probably best illustrated by looking at the decay shapes of the two functions. The shape of the KWW function is determined by the stretching exponent β, which for the presented examples lies in the range of 0.6. This coincides with the earlier theoretical result that for large times and small trap densities, the decay is governed by a KWW function with $\beta = 3/5$.[14,21] In contrast, the shape of the TSE function does not change for different parameter sets. It can therefore stand as a characteristic fingerprint for this special kind of relaxation process. Whether one or the other function yields the best description for a given data set may be estimated with the help of difference plots, as shown in Fig. 2. This method may even be applied if original data are missing, and only a KWW fit is available to which a TSE model can then in turn be fitted.

Despite the apparent advantages of the presented TSE description, in many practical cases relaxations occur which are described by KWW decays with $\beta \neq 3/5$.[5–9,22] On the microscopic scale, these may be caused by superpositions of TSE decays with different parameter sets within the same system, such as modulated defect densities.[22,23] Here, specific TSE decays in different spatial regions cannot be resolved by macroscopic experimental techniques. More complex situations include multiple (intermediate) trapping and releasing processes, possibly involving different defect levels within one system, as well as optical excitations out of defect centers, and site-correlation effects.[5,8,24] Although these more complex phenomena are not directly covered by the TSE model, the microscopic approach outlined in this Brief Report appears to be a promising tool for their description.

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