

Study of Generation-recombination Processes by the Graph Theory

E. V. Kanaki¹, S. Zh. Karazhanov^{2,*}

¹Physical-Technical Institute, 2B-Mavlyanova str., 700084, Tashkent, Uzbekistan

²Institute for Energy technology, 2027 Kjeller, Norway

Abstract Generation-recombination (GR) processes of electrons and holes play important role in solar cells by controlling carrier lifetime and influencing on device performance. Commonly kinetic theory is used to study the processes. The aim of the article is to use graph theory and represent the GR processes in schematic form: defect states by dots and transitions between them by arcs. The centers of recombination have been classified within the definitions of the graph theory. An equation for the stationary distribution function of defects on states has been derived without constructing the system of kinetic equations. The theory can be helpful for simplification of the model of recombination through point defects. It should be based not only on smallest magnitude of the transition probability, but also on the role of the transition in the digraph of states. Distribution function of defects on their states has been found for asymptotic high injection level. We have derived the equation for the rate of the GR processes, which is universal for all types of point defects. Models of inertial and static behavior of the recombination centers have been discussed and the equations for them have been derived.

Keywords Generation-recombination Processes, Charge Carrier Lifetime, Defects, Semiconductor Materials, Graph Theory

1. Introduction

Graph theory was formed in XVIII century and its origin was related to mathematical puzzles. So, for a long time the doctrine about graphs was considered as a not serious topic because its practical applications were related only to games and entertainments. In this sense destiny of the graph theory can be compared to that of the probability theory, which initially was also considered with respect to games of chance. In XX century graphs have attracted attention of topologists and are considered as one of the chapters of topology, which was then one of the topics of mathematics and it interested only narrow range of readers. Since the time, there have been significant changes. Graph theory has been found to be important for solution of many problems of practice. The theory has found wide range of applications in different fields of science such as electrotechnics, electromechanics, radioelectronics, physics, chemistry, geodesy, sociology, economics etc. Literature on the topic increases with fastest rate (see e.g. Refs. ¹⁻¹⁸). There are specialized journals such as "Journal of the graph theory", and "Journal of graph algorithms and applications". Specialized conferences are held on the subject. The reason for such a high interest to the graph theory can be explained

by possibility of formulation and solution of problems in terminology and concepts of graphs, which are aggregation of dots connected with each other by lines. If the dots (vertexes of the graph) are identified as functional or constructional components and lines (arcs or edges of the graph) are identified as the cause and reason type relation, then the process or phenomena, system of equations or matrixes can be replaced by graphs, which consists of all the external and internal relations between objects of the phenomena or between variables in the system of equations. Such a graph model allows to establish clear relation between structure of the system and its quantitative characteristics, and to apply general methods to solution of the problems.

1.1. Applications of the Graph Theory

Currently graph theory is widely used in many fields of science and technology. One of them is programming⁷⁻¹⁰. Here there is an important problem of segmentation of programs to minimize exchanges between the operative and external memories. In graph theory the problem is related to decomposition of graphs. Another problem of optimal distribution of different program blocks requires minimization of expected number of transfer of controlling, which can be solved by constructing the Hamilton cycle in the graph theory. Also, there are some other problems such as itinerary, modelling of the data transfer and distribution of information in the communication systems, which can be solved using the graph theory.

* Corresponding author:

smagulk@ife.no (S. Zh. Karazhanov)

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Automation of designing of the microelectronic computational structures and systems can also be considered from the point of view of the graph theory. In the topic related to recognizing of the graph isomorphism, finding all of the ways, optimal decomposition of the graphs, construction of the minimal connecting trees etc are very important.

Graph theory has found an application also in description of mechanical movement of matter (see e.g. Refs.^{11,12}). It is found to be a convenient tool for presentation and construction of the system of equations. Graph models have been found for systems described in terminology of energy and power, which include the Lagrange equation and generalized coordinates. The models allow to understand both energetic structure of a system and its functional behaviour including non-linearity and to withdraw the equations in the state space.

In hydrodynamic systems graph theory allowed to replace description of hydraulic systems with distributed parameters with those of point ones¹³. In geodesy¹⁴ it allowed to make topological classification of geodesic constructions and to find possibility of description of the geodesic network structure by the Boolean algebra.

Graphs have also been used for construction of models of the human-heart-vessel system with distributed parameters¹⁵. The models include the heart, arterial, capillary and vein parts of both system and lung blood circulation. Due to universality of the graph theory language, the models are functionally soft and can be modified. One of the models is body movement caused by blood flow of human mechanically separated from the earth. It provides the possibility for indirect determining the characteristics of the heart operation.

Electrical network can be described as aggregation of elements and nodes connecting the elements. It can be abstracted to the concept of graphs of electrical networks with multipole elements. Basic concepts of the mathematical graph theory for such graphs have already been developed, which have found application in analysis of networks by topological methods¹⁶. Mathematical tool of the scheme multiplicities, introduced for description of graphs, provided formalization of the procedure for analysis alleviating construction of its algorithm and further improvements in computational designing of electrical networks.

Graph theory is actively used in chemistry, biology and physics (see e.g. Refs.^{17, 18}). If atoms are presented as vertexes of a graph and lines connecting the vertexes as relations between them, then one gets the graph presentation of molecular or crystal structure of matter. This is the well-known classic language of structural chemistry and crystallography.

Denoting the matters by dots and reactions between them by lines, one comes to graphical presentation of chemical reactions, widely used in chemistry, biology and physics¹⁷⁻²⁰. Similarly, if dots correspond to defects and lines to the defect transformations, then one can get the photo-, thermal- and recombination-stimulated defect reactions²¹ well known in

modern solid state physics. If dots identify the different charge or configuration states of defects and lines identify defect transitions between the states, such a graph describe GR processes in semiconductors²²⁻²⁷. If variables are depicted by dots and relations between the variables by lines, then one gets the system of linear equations describing the chemical, biological or physical etc system. Often the reaction schemes have been depicted without knowing that this is the graph of the complicated phenomena.

Conception of the scientific field "Synergetics" appeared at intersection of many other fields such as chemistry, biology, physics etc resulted in the necessity to study complex behaviour of non-linear dynamic systems. The problem was to define the mechanism and parameters, which are responsible for spontaneous formation of multiple stationary states, periodic and chaotic oscillations in point and distributed systems. Graph theory has found application in this field also^{17,18}. Distinct from graphs of linear systems, which identify vertexes as matters and arcs as reactions, graphs of non-linear phenomena systems are bipartite, which contains two types of vertexes: matters and reactions. Arcs (or edges) of a bipartite graph indicates that some matter is formed or expended during the reaction.

In the above-listed kinetic problems, graph theory provided the possibility to find stationary concentration of intermediate matters, stationary velocity of complicated reaction, to write down the characteristic polynomial, which is necessary in studying the relaxation processes, and to analyse the number of independent variables of the stationary kinetic equations etc.^{17,18}.

Solution of many problems in chemistry and physics of polymers is simplified significantly if they are formulated in terminology of the graph theory¹⁷. It is especially effective in consideration of the branched polymers^{28, 29}. Note that application of graph theory is not limited to the above list. Further, we will concentrate attention to GR processes.

1.2. Motivation in Using the Graph Theory for the Study of Generation-recombination Processes

As different schemes, matrixes, systems of equations are used in investigation of GR processes, graph theory, which studies topological properties of schemes, can find application in this field also. Together with the usually used kinetic approach it can be a new effective theoretical tool in this field. It is interesting not only because of its novelty in applying in GR processes, but also due to its importance in simplification of the system of kinetic equations, finding asymptotical values of the distribution function, and because it has brought us to new results. It is not a principally new method, but it amplifies significantly and extends the kinetic approach leading the GR processes to maximal formalization. Application of the graph theory in this field allows to present the results analytically and to supply with topological picture of the relations between variables, which in some cases can lead to new results.

Earlier, we have reported our preliminary results about using the graph theory in investigation of GR processes²⁶. In

addition to it, in the present article we found more interesting results, which demonstrate power of the graph theory as a new mathematical tool and its prospects in physics of semiconductors. In addition to the kinetic approach, graph theory can be an effective tool for analysis and solution of a number of problems.

As the graph theory is not well known to wide range of readers in the field of physics of semiconductors and currently there are no systematic studies on application of the theory to GR processes, the authors pursue the following goals: (i) to acquire specialists in the field of physics of semiconductors with basic concepts of the graph theory, with its methods, definitions and terminology; (ii) to demonstrate on examples how the theory can be used for GR processes and to present the results obtained systematically. The most serious limitation of this paper is that it covers consideration of only point defects. Recombination through linear and bulk defects, nanosized objects, Boltzmann kinetic equations are not considered. These limitations emphasizes importance and actuality of the results presented in this review.

During study of the graph theory our attention was turned to search of possibility of direct application of existing solutions and basic concepts of the graph theory to problems of GR processes. Therefore, some definitions and theorems have been used without proof and justification, referring to corresponding sources. Upon presentation of the results, usual terminologies of the graph and recombination theories have been used. So, no preliminary knowledge of the graph theory is required, since all necessary ones are in the paper.

1.3. GR Processes Through Point Defects

Prime task in investigation of influence of defects on physical properties of semiconductors is finding the distribution function of defects on states and GR rate, which depend on temperature, carrier injection, illumination, etc. This is because many electrical properties of semiconductors, in particular, specific (photo-) conductivity, carrier recombination rate and lifetime, intensity and spectral distribution of luminescence, depend on the number of defects in that or other state. Usually for this purpose, system of kinetic equations for free carrier and defect concentrations is constructed (see, e.g., Refs.^{22,23,30-36}). By solving the system, one can get the required distribution function and recombination rate. Theory of the GR processes in semiconductors is first developed by Shockley-Read³² and Hall³¹ for the simplest defect with one energy level in the band gap and two charge states. Since then the theory has been extended for more complicated models of point defects: multiple charge defects without excited states³²⁻³⁴, two-charged defects with one excited state^{22,34,36}, four charge defects without excited states and three-charged defects with an excited state^{24,37-40}, bistable defects⁴¹, hypothetical model of metastable defects⁴². First systematic investigation of the GR problem is done in the book by Landsberg²². The above studies are based on kinetic theory, which is easy to use for simple defects with two or three states in the band gap. However, it is more complicated for defects with more

number of charge states and different number of configurations and/or excited states. Analysis of literature shows that many semiconductors may contain different types of complicated defects, which modulate carrier lifetime and electrical properties of the material. Some examples for Si are, e.g., boron-oxygen complex Si^{43} , donor-H complex⁴⁴, which are responsible for degradation of carrier lifetime in solar cells, metastable oxygen - silicon interstitial complex in crystalline silicon⁴⁵, metastable and bistable defects⁴⁶, etc. Theoretical analysis of such system by using the kinetic theory might become a time consuming work and having an alternative method is important. Also, the rate of GR processes is commonly estimated by equation $U = \Delta n(\Delta p)/\tau_{n,p}$, where $\Delta n(\Delta p)$ and $\tau_{n,p}$ are the excess electron(hole) concentration and lifetime, respectively, which can be measured experimentally. Here, the approximation $U = \Delta n(\Delta p)/\tau_{n,p}$ has been derived from the theory by Shockley-Read³⁰ and Hall³¹. However the question as to whether the equation is valid for all models of recombination through point defects is open. In this article, we will use graph theory and solve these challenges. Applying a new method for study of a process always is interesting and might lead to some exciting results. In particular, by using the graph theory we have approached the GR processes from different angle.

2. Methods

2.1. Assumptions

The defects can be in different charge states or configurations. The origin of the defects can be different: intrinsic, extrinsic defects, or their complexes. The defect can have any number of configurations and charge states. The defects should be independent each from other. They should not interchange by carriers by tunnelling and should not interact through electrical and magnetic fields or mechanical stresses of a distorted lattice. It is assumed that the semiconductor is non-degenerate and that influence of GR processes determined by materials properties such as the band-to-band or Auger recombination can be neglected. Stationary state of the system is suggested to be stable. Dynamic equilibrium is assumed in the transitions between different states. Also, we did not account for the processes of defect generation, annihilation, and migration.

2.2. Kinetic Theory

Kinetic theory stands²² at the very heart in the study of the GR processes taking place via, in particular, point defects of net concentration N_{tot} . The defect is supposed to be in $i=1, \dots, M$ states with the concentration N_i in the i -th state, so that $M > N_{tot}$ [Fig. 1]. Transition from one state, i , into another one, j , is denoted as $i \rightarrow j$ characterized by the weight, ω_{ij} , which is equal to the probability of the transition per unit time. Kinetics of the concentration of the defects can be described by the following equations

$$\frac{dN_i}{dt} = - \left(\sum_{j \neq i} \omega_{ij} \right) N_i + \sum_{j \neq i} \omega_{ji} N_j \quad (i=1 \dots M), \quad (1)$$

$$\sum_{i=1}^M N_i = N_{\text{tot}}, \quad (2)$$

The first term in the right hand side of the Eq. (1) gives the net rate of transitions of defects from the state i into the state j per unit volume, and the second term is equal to the rate of reverse transition of the defect into the state i from j . Dividing Eqs. (1) and (2) to N_{tot} one can find the fraction of the defects corresponding to each of the states $F_i = N_i / N_{\text{tot}}$ to be called hereafter as the stationary distribution function

$$- \left(\sum_{j \neq i} \omega_{ij} \right) F_i + \sum_{j \neq i} \omega_{ji} F_j = 0 \quad (i=1, \dots, M), \quad (3)$$

$$\sum_{i=1}^M F_i = 1. \quad (4)$$

The above Eqs. (1)-(4) allows to calculate the rate of GR processes for electrons U_n and holes U_p , which in stationary case is equal to each other $U_n = U_p$. Here $U_n(U_p)$ can be calculated as the difference of the capture rate of free electron(hole) by the defect from that of the thermal emission rate. Knowledge of U_n and U_p allows to calculate

carrier lifetimes from the standard equations

$$\tau_n = \frac{\Delta n}{U}, \quad (5)$$

$$\tau_p = \frac{\Delta p}{U}, \quad (6)$$

respectively. Here $\Delta n = n - n_0$ and $\Delta p = p - p_0$ are the excess concentrations, n and p are the net concentrations, and n_0 and p_0 are the equilibrium concentrations of free electrons and holes. The relation between them can be found from the electro-neutrality requirement

$$p = n \pm N_{a,d} \pm N_i. \quad (7)$$

Here $N_{a,d}$ stands for the concentration of shallow acceptors and donors, respectively. N_i is the concentration of the recombination center. The (+) sign comes if the defect is negatively charged and (-), if it is positively charged.

2.2.1. Theory of Recombination by Shockley-Read-Hall

One of the examples we consider is the theory developed by Shockley and Read³⁰ as well as by Hall³¹ (SRH). In the theory transformations of the defect from one charge state into another one can be denoted as $1 \leftrightarrow 2$ and $2 \leftrightarrow 1$ (Fig. 1(a)). Each of the transitions $i \rightarrow j$ in the Fig. 1(a) have been marked by corresponding weight ω_{ij}

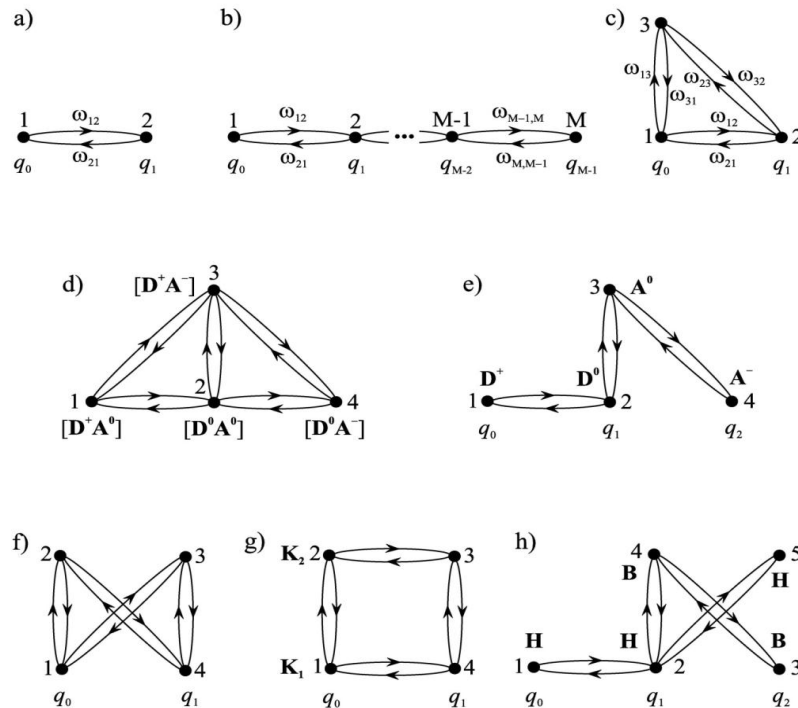


Figure 1. Digraphs of states for defects with (a) two-charge and (b) M-charge without excited states, (c) two-charge defect with one excited state, (d) donor-acceptor pairs with three different charge states, (e) three-charge defects with one excited state, (f) two-charge defect with two excited states, (g) two-charge bistable defect and (h) three-charge U -centers in n-Si. Each vertex of the digraphs corresponds to a particular quantum state of the defects and arcs correspond to the allowed transitions between these states. Weights of the transitions ω_{ij} are equal to the probabilities of the corresponding transitions per unit time. Vertices of a digraph, posed along one vertical, concern to the same charge state of a defect. The lowest vertex corresponds to the ground state whereas the highest ones denote excited states. The digraphs are symmetric, which means that transition described by the arc $i \rightarrow j$ of the digraph contains its counter arc $j \rightarrow i$. Also, the digraphs are strong, which means that all their vertices are mutually accessible

$$\omega_{12} = C_n^{12} n + E_p^{12}, \quad \omega_{21} = C_p^{21} p + E_n^{21}. \quad (8)$$

Here $C_{n,p}^{ij}$ and $E_{n,p}^{ij}$ are the specific probabilities of carrier capture by the defect and of emission from the defect level into the allowed bands. The fraction F of a defect with an electron and recombination rate U found from Eqs. (1)-(6) at steady state conditions are at the form

$$F = \frac{C_n n - C_p p_1}{C_n(n + n_1) + C_p(p + p_1)}, \quad (9)$$

$$U = \frac{C_n C_p N_i (np - n_i^2)}{C_n(n + n_1) + C_p(p + p_1)}. \quad (10)$$

2.2.2. Theory of Recombination Via Bistable Defects

Upon transitions of bistable defects $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$ (Fig. 1(b)) the charge of the defects is conserved and the defect configuration changes, whereas upon $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$ the charge state of the defect changes without changing of the configuration. The other possible transitions $1 \leftrightarrow 4$ and $2 \leftrightarrow 3$, which would be accompanied by transformation of both configuration and charge, have been neglected. The reason is that we have not seen any experimental evidence for existence of such bistable defects in Si. Weights of each of the transitions $i \rightarrow j$ denoted by ω_{ij} [Fig. 1 (d)] are

$$\omega_{34} = C_n^{34} n + E_p^{34}, \quad \omega_{43} = C_p^{43} p + E_n^{43}, \quad \omega_{31} = \exp(E_0 / kT) \omega_{13}, \quad \omega_{42} = \exp(E_1 / kT) \omega_{24}. \quad (11)$$

Here ω_{13} , ω_{31} , ω_{24} and ω_{42} are the probabilities of defect transitions from $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$, respectively. E_0 and E_1 are the activation energies of configuration transformations of the defect without an electron and that with an electron, kT is the thermal energy.

2.3. Elements of the Graph Theory

The following definitions might be important to link the graph theory with the generation recombination processes through the ensemble of identical and independent from each other point defects, which can be in M different quantum states $|i\rangle$ ($i = 1, \dots, M$). These definitions can be found in Refs. 1-3, 5-7, 11, 12, 17.

Definition 1. A graph is a mathematical structure composed of points called **vertices**, which are the fundamental building blocks of graphs. The vertices are connected by lines called **edges** or **arcs**. In GR processes each state $|i\rangle$ of a defect ($i = 1, \dots, M$) corresponds to a **vertex** i of the graph. The arc $i \rightarrow j$, connecting the defect states i and j , indicates an allowed transition from the state $|i\rangle$ to the state $|j\rangle$ probability of the transitions between the states $|i\rangle$ and $|j\rangle$ per unit time corresponds to the weight ω_{ij} ($[T^{-1}]$) of the arc $i \rightarrow j$. If there are several competing mechanisms of transition of the defect from the state $|i\rangle$ to the state $|j\rangle$ one can draw several arcs coming out from the vertex i to the vertex j , thus forming the so-called multiple

arcs¹⁻⁴. Each of the arcs should be assigned the weight $\omega_{ij}^{(\alpha)}$, which is equal to the transition probability by the corresponding mechanism " α ". There might exist also loops, which are the arcs going out of a vertex and coming back into it without connecting to any other vertex. Existence of a loop indicates the possibility of static influence of defects on electronic transitions in the system, which we will discuss later. Some mechanisms of static involvement of defects are below.

Definition 2. The defect states and transitions between them have been presented pictorially, which we call the **digraph of states G**. There are two types of graphs: **undirected graph**, consisting of unordered vertices with a set of edges and **directed graph**, which consists of ordered vertices and a set of edges. A digraph G can be said to be **strongly connected** if all its vertices are mutually reachable. Important feature of the strong digraphs is that for each its vertex there exist at least one **directed tree** covering the digraph and growing into this vertex. Physically it means that the defect state in any state i ($i = 1, \dots, M$) can reach any of the other states. Fig. 1 presents examples of such strongly connected digraphs. The case of **weakly connected digraph G** will be considered separately.

Definition 3. One of the widely used definitions in the graph theory is called **tree**, which is an undirected graph in which any two vertices are connected by *exactly one* simple path. In other words, any connected graph without cycles is a tree. A **forest** is an undirected graph, all of whose connected components are trees; in other words, the graph consists of a disjoint union of trees. A **directed tree** is a directed graph which would be a tree if the directions on the edges were ignored. Some authors restrict the phrase to the case where the edges are all directed towards a particular vertex, or all directed away from a particular vertex. A tree is called a **rooted tree** if one vertex has been designated the **root**, in which case the edges have a natural orientation, towards or away from the root.

Definition 4. The directed tree $T^{(i)}$ covering the M -vertex digraph G and growing into its vertex i is defined as the subgraph in G which includes all the M vertexes and $(M-1)$ arcs in such a manner that starting from any vertex other than i and moving along these arcs one necessarily comes into the vertex i (to be called "the root" of the tree $T^{(i)}$).

To show that the results of the kinetic approach can easily be obtained using the graph theory, we will analyse the kinetic equations (1) and (2), describing the kinetics of distribution of defects on their states. Since the defects comprising the ensemble are assumed to be independent, the probabilities of transitions ω_{ij} do not depend on F_i explicitly. Therefore, from the mathematical point of view the Eqs (3)-(4) are the system of linear inhomogeneous equations for F_i ($i = 1, \dots, M$). Such a system of equations can be solved by the graph theory. Below we show that the solution of this system of equations can be constructed with the help of a digraph of states G . We will consider a strongly connected digraph G with vertices, which are mutually reachable. In Fig. 2 we show example of an eight-vertex digraph G with

loops $4 \rightarrow 4$ and $5 \rightarrow 5$ and multiple arcs $4 \xrightarrow{(a,b,c)} 1$ and $2 \xrightarrow{(a,b)} 5$ and covered with a tree $T^{(j)} = (5 \rightarrow 2 \rightarrow 1) \& (3 \rightarrow 1) \& (6 \rightarrow 4 \rightarrow 1) \& (7 \rightarrow 4) \& (8 \rightarrow 4)$ that grows into the vertex 1. If there are several trees covering a digraph G and growing into its vertex i , a subscript is used in the notation $T_\alpha^{(i)}$ to distinguish them each from other. The trees are considered as different when the sets of their arcs do not coincide. Each tree $T_\alpha^{(i)}$ will be assigned the weight $[T_\alpha^{(i)}]$, which equals to the product of the weights of all its arcs:

$$[T_\alpha^{(i)}] \equiv \prod_{j \rightarrow k \in T_\alpha^{(i)}} \omega_{jk}. \quad (12)$$

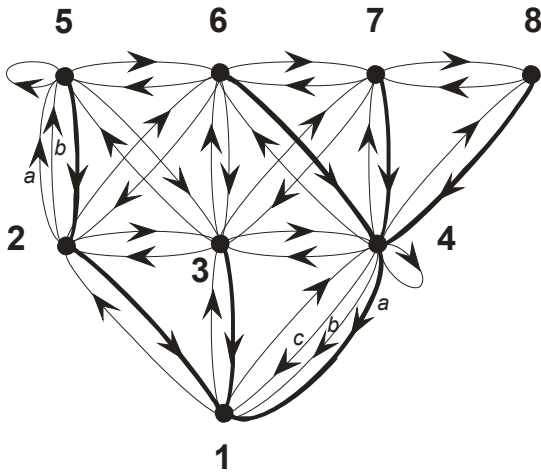


Figure 2. The digraph G . One of the trees $T^{(j)}$ is selected that covers the digraph and grows into the 1st vertex. Arcs not included into the tree are plotted by dots. The tree $T^{(j)} = (7 \rightarrow 4) \& (8 \rightarrow 4) \& (5 \rightarrow 2 \rightarrow 1) \& (3 \rightarrow 1) \& (6 \rightarrow 4 \rightarrow 1)$ consists of seven arcs linking all eight vertices of the digraph G in such a manner that, moving along these arcs from any vertex, one inevitably comes into the root vertex 1 and leaving the vertex is not possible. This example shows the important features of “growing into” type trees. It has no bifurcations, i.e. there are no groups of two or more arcs issued from the same vertex. It does not contain cycles, including loops. Deleting any arc from a tree, but saving all its vertices, leads to breaking of the tree into two fragments, which are also the growing into type trees. Thus, if the arc $4 \rightarrow 1$, e.g., is excluded from the tree $T^{(j)}$, then one can get the trees $(5 \rightarrow 2 \rightarrow 1) \& (3 \rightarrow 1)$ and $(6 \rightarrow 4) \& (7 \rightarrow 4) \& (8 \rightarrow 4)$ growing into the 1st and 4th vertices, respectively. Note that the sole vertex may be considered as a trivial case of the trees. The addition to a tree covering a digraph G of one more arc of G creates a cycle and/or a bifurcation. For example, if $T^{(j)}$ will be added with the arc $1 \rightarrow 2$, then the cycle $C = 1 \rightarrow 2 \rightarrow 1$ will appear with two trees growing into its vertices: $5 \rightarrow 2$ and $(6 \rightarrow 4) \& (7 \rightarrow 4) \& (8 \rightarrow 4 \rightarrow 1) \& (3 \rightarrow 1)$. Such constructions are known as the functional graphs

Each vertex i will be assigned a tree-weight $[i]$, which is equal to the sum of the weights of all trees covering the digraph G and growing into the vertex i :

$$[i] \equiv \sum_{\alpha} [T_\alpha^{(i)}] \quad (i = 1, \dots, M). \quad (13)$$

The total tree-weight of all vertices of a digraph G will be designated as $[G]$:

$$[G] \equiv \sum_{i=1}^M [i]. \quad (14)$$

Then, the portion of defects F_i in the i -th state in the Eq. (3) and (4) in the steady state conditions can be expressed as the specific tree-weight of the i -th vertex of the digraph G

$$F_i = [i]/[G]. \quad (i = 1, \dots, M). \quad (15)$$

In fact this is the solution of the Eqs. (3)-(4). As it will be shown in Appendix A, the Eq. (15) can be immediately deduced from the matrix-tree theorem improved in Ref.[2].

3. Results. Non-Equilibrium Distribution Function

3.1. Classification of Recombination Centers According to the Graph Theory

As noted earlier, recombination centers can be in several states differing each from other by charge and excited states or configuration and transition between them is possible during GR processes. By one vertex corresponds to each state of the defect. Below we will perform classification of the recombination centers according to the graph theory, which is based on the total number of states the defects.

3.1.1. Defects with two Charge States: Bivertex Digraph

The simplest type of defects can be in one of the two charge states: neutral and positively charged or neutral and negatively charged. Theory of recombination through such defects was developed by Shockley and Read³⁰, and Hall³¹ for non-degenerate case and without accounting for the Auger effects. Digraph corresponding to such a defect is shown in Fig.1 (a) and can be called as bivertex digraph. The vertex 1 corresponds, for example, to the defect in charge state q_0 without an electron whereas the vertex 2 corresponds to the defect with one trapped electron and having, therefore, the charge $q_1 = q_0 - 1$. If one neglects the multi-particle mechanisms of transitions the probability ω_{12} of capture of an electron by the defect and probability ω_{21} of emission of an electron from the defect are: $\omega_{12} = C_n n + E_p$ and $\omega_{21} = C_p p + E_n$. One can take the mechanism of Auger recombination into account by incorporating the terms like $T^{ij} n^\xi p^\zeta$ into the probabilities ω_{ij} ; in non-degeneracy case the parameters ξ and ζ are integers and are equal to the number of free electrons and holes participating in the transition, respectively (see, for example,²²). In the degenerated case the parameters can be fractional⁴⁷; the coefficients $T^{ij} [L^{3(\xi+\zeta)} T^{-1}]$ are determined by the nature of a defect and its electronic states, and also by mechanisms of energy dissipation.

3.1.2. A Defect with net M-charged States Without Excited States: M-vertex Digraph

The digraph, corresponding to a defect, which can be in multiple charged states and does not have excited states, is shown in Fig.1b. It can be called as M-vertex graph with M

vertices corresponding to different charge states. The i -th ($i=1, \dots, M$) vertex is supposed to correspond to the defect with $(i-1)$ captured electrons, so that $q_i = q_{i-1} - 1$. Charge of the defect in the state 1 is designated as q_0 . In non-degenerate case upon neglecting the multi-particle effects the transition probability of the defect from the state i into the state $i+1$ is determined by the probabilities of capture of an electron from the conduction and valence bands $\omega_{i,i+1} = C_n^{i,i+1} n + E_p^{i,i+1}$. For reverse transitions it is defined by probabilities of departure of an electron into allowed bands: $\omega_{i+1,i} = C_p^{i+1,i} p + E_n^{i+1,i}$ ($i=1, \dots, M-1$). GR processes via such defects were studied^{32,33,35} by the kinetic theory.

3.1.3. A Defect with Two-charged and One Excited States: Three-vertex Digraph

Such a defect can be in two charged states. In one of them it has one excited state. In graph theory such a defect can be plotted as a three-vertex digraph [Fig. 1c]. The vertices 2 and 1 correspond to the ground states of the defect. In one of them it contains one electron, in the other state it has no electron. The vertex 3 corresponds to the excited state with the same charge as the state 1. Then the transitions $1 \leftrightarrow 3$ correspond to the intra-center ones. Distinct from other transitions, charge state of the defect will not be changed. Theory of GR processes through such defects, when the excited state is an exciton bound to a defect has been studied in Ref.[34]. Similar model was proposed in correlation mechanism of recombination³⁶.

3.1.4. Defects Described by the Four-vertex Digraphs

Defects, which can be in four-charge states without excited states can be described by the four-vertex digraph. It can be regarded as a particular case of the multiple charged defect described in Subsection 3.1.2 for when $M=4$. Below we list some examples of such defects. One of them is the defect with three different charged states and with one excited state. The other one possesses two charged states with one excited state for the each charge state or both excited states at one of the charge states. Donor-acceptor [DA] pair consisting of closely situated donor (D) and acceptor (A) centers with allowed electronic exchange between D and A can be the third example of the three-charge defect with one excited state. The fourth example is the solitary pair, which cannot influence on each other because of large distance between them. The appropriate digraph is shown in Fig. 1d. The vertex 1 corresponds to the positively charged pair [D⁺A⁰]. The vertices 2 and 3 are the neutral states of a pair [D⁰A⁰] and [D⁺A⁻] respectively. The vertex 4 is a negatively charged pair [D⁰A⁻]. Transitions between the states 2 and 3 are the intra-centers ones, whereas other transitions are the carrier exchange between the components of the pair and allowed bands.

One more example of the defects with three-charged states and one excited state is the U^- -center⁴⁰. Digraph for the defects is shown in Fig. 1e. Vertex 1 is the positively charged state, which is designated as D⁺ in [Ref.40]. Vertex 2 and 3

correspond to the neutral states of the defect D⁰ and A⁰, which differ each from other by the configuration. Vertex 4 are the negatively charged state of the defect A⁻. Transitions $2 \leftrightarrow 3$ between the neutral states D⁰ and A⁰ correspond to the transformation of the configuration of the defect whereas the remaining transitions are the electronic exchange of the defect with allowed bands.

Theory of recombination through defects with two charges in the ground and excited states was studied in Ref. [37]. Afterwards the model of cascade recombination was studied in a number of other papers²². Fig. 1f presents digraph for the defect with two charge states. The defect in its empty ground state 1 can capture an electron from the conduction band into the upper level, and be transformed into the filled excited state 3. From the state it can relax into the ground state 4, filled with two electrons. Being in this state it gets the possibility to capture a hole into the lower level, located closer to the top of the valence band, i.e. to pass the electron with smaller energy to the valence band and to move thus into an empty excited state 2. Then it can be transformed into the state 1 due to transition of an electron from the upper to the lower level of the defect. Together with the above-mentioned transitions reverse transitions have been taken into account.

Recombination theory through the two-charge bistable defects with one excited state for each charge state is described in Refs. [41,48]. It should be noted that many defect complexes in Si such as, e.g., Fe₁B_s, Fe₁Al_s, Fe₁Ga_s, Fe₁In_s, B-O, etc. are the examples of the bistable defects. Digraph for the defects is shown in Fig. 1g. Vertices 1 and 2 correspond to the empty defects with charge q_0 in space configurations Q₁ and Q₂. The vertices 4 and 3 correspond to the defects in the same configurations with an additional electron and, therefore, with the charge $q_1 = q_0 - 1$. For such a defect in silicon, for example Fe₁Al_s, the two charge states are Fe₁²⁺Al_s⁻ and Fe₁⁺Al_s⁻ in two possible orientations along the direction <111> and <100> (Ref.[49]). Therefore, the transitions $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$ are the transformations of the configuration of the defect without changing the charge state, whereas $1 \leftrightarrow 4$ and $2 \leftrightarrow 3$ are accompanied by carrier exchange of the defect with allowed bands, but without changing the reconfiguration. Note that changing the charge state of a defect simultaneously with its configuration (i.e. transitions immediately between the states 1 and 3 or 2 and 4), is considered as improbable event and in Ref.⁴¹ it was not taken into account.

3.1.5. Defects with Five States: Five-vertex Digraph

There are several types of defects, which can belong to the five-vertex graphs. One of them is the defect, which can be in five charged states and without excited states. The other one is the defect with two charge states and three excited states. Below we will focus on an example of the defect with three charge and two excited states⁴⁹ in the study of the U^- -centers. Hydrogen and thermal donors in Si can be regarded as examples. The digraph of states is shown in Fig. 1h. The defect in the state 1 is double positively charged

($q_0 = +2$). By capturing an electron it passes into a single-charged state 2 ($q_1 = +1$). From the state it proceeds either into the state 4 with the same charge q_1 but in another configuration, or, by capturing an additional electron into the neutral state 5 ($q_2 = 0$). In the state 4 the defect can capture an electron and proceed into the neutral state 3, which differs from the state 5 by space configuration. In Ref.[49] configuration of the states 4 and 3 are identical (designated as “**B**-configuration”) and that of the states 1, 2 and 5 are also identical (“**H**-configuration”). So, the transitions between the states 2 and 4 are related to change of configuration of the defect whereas the remaining ones are accompanied by changing of charge state of the defect because of the electronic exchange between the defect and allowed bands occurring without changes of the configuration.

3.2. Distribution of Defect Concentration on States: Digraph of States

As mentioned above, at steady state conditions the portion of defects F_i in the i -th state can be estimated as the specific tree-weight of the i -th vertex of the digraph $\mathbf{G}$ [Eq. (15)]. The Eq. (15) can be immediately deduced from the matrix-tree theorem proved² by W. Tutte[Appendix A] without constructing the system of kinetic equations. We shall also reveal the informal aspect of the result by showing that it is only the tree form of the state weights[Eqs. (12) and (13)] that is capable of providing the balance of flows in the stationary system at arbitrary variations of transition probabilities. So, by the tree-weight rule[Eqs. (12)-(15)] it becomes possible to obtain F_i from the digraph of defect states $\mathbf{G}$.

First of all, let us give the comprehensive description of structure of the equation for F_i . From the properties of a M -vertex tree $\mathbf{T}^{(i)}$ growing into the i -th vertex it follows that its weight $[\mathbf{T}^{(i)}]$ [Eq. (12)] consists of $(M-1)$ terms ω_{jk} . Among them there are no weights with equal indexes ω_{jj} , since the tree has no loops $i \rightarrow i$, no products of weights with equal values of the first index like $\omega_{jk}\omega_{jl}$, since the tree of the “growing into” type has no bifurcations like $(j \rightarrow k) \& (j \rightarrow l)$ and, no factors with cyclic values of indices, i.e. the factors like $\omega_{jk}\omega_{kl}$, $\omega_{jk}\omega_{kl}\omega_{lj}$, etc., since the tree has no cycles like $j \rightarrow k \rightarrow j$, $(j \rightarrow k \rightarrow l \rightarrow j)$, etc. Under these conditions being fulfilled, among the values of the second index of the factors ω_{jk} there will necessarily be such a one, which is not among the values of the first index and this is the value which corresponds to the root vertex i of a tree $\mathbf{T}^{(i)}$. For example, the product $\omega_{52}\omega_{21}\omega_{31}\omega_{64}\omega_{41}\omega_{74}\omega_{84}$ in Fig. 2 fulfils all the above requirements and hence represents the weight of the tree with eight vertices, which grows into the 1st vertex. The product consists of the seven terms ω_{jk} . Based on this equation one can easily get the visual image of the tree: since it consists of the weights of the arcs $5 \rightarrow 2$, $2 \rightarrow 1$, $3 \rightarrow 1$, $6 \rightarrow 4$, $4 \rightarrow 1$, $7 \rightarrow 4$ and $8 \rightarrow 4$, we deal with the tree $\mathbf{T}^{(1)} = (5 \rightarrow 2 \rightarrow 1) \& (3 \rightarrow 1) \& (6 \rightarrow 4 \rightarrow 1) \& (7 \rightarrow 4) \& (8 \rightarrow 4)$ that has been depicted in Fig.2. So, the above description fully determines the structure of each addend in the numerator and denominator of the Eq. (6). Number of addends in the

numerator in Eq. (6) depends on features of the scheme of allowed transitions and can be found with help of the square matrix $\mathbf{K} = \|k_{ij}\|$ of order M . Each diagonal element k_{ii} of the matrix is equal to the number of arcs issued from the vertex i and the off-diagonal element k_{ij} ($i \neq j$) is equal to the number of arcs coming from the vertex j into the vertex i taken with minus sign. Loops of the digraph $\mathbf{G}$ are not taken into account. Cofactor of any element in the i -th column of the $\mathbf{K}$ -matrix gives the number of the trees covering $\mathbf{G}$ and growing into the i -th vertex (see, e.g., Ref. [1]). It gives the number of addends in the numerator in the equation for F_i . Number of addends in the denominator of the Eq. (15) is equal to the total number of addends in the numerators for all $i = 1, \dots, M$.

From the above description it is seen that the structure of Eq. (15) for F_i bears a strong resemblance to the equation for the probability of a complex event which may happen by several mutually exclusive ways. Each way consists of a few independent steps: each such step is a certain transition of a defect from one state into another one, and each way is a bunch of the transitions forming a certain tree. So the weight of the tree $[\mathbf{T}_\alpha^{(i)}]$ is the probability of reaching the final state i by the certain “way” $\mathbf{T}_\alpha^{(i)}$, which is the product of the probabilities of “steps” ω_{jk} constituting this “way”; the denominator $[\mathbf{G}]$ in Eq.(15) is simply a normalizing factor. Unfortunately, we failed to find the physical reasons for this remarkable resemblance.

The GR processes fulfil the principle of detailed balance, i.e. obey the Gibbs statistics. It means that at thermodynamic equilibrium case each transition of a defect from the state i to the state j described by the arc $i \rightarrow j$ is balanced by reverse one corresponding to the arc $j \rightarrow i$. By other words, the GR processes of electrons and holes through point defects should be described by symmetric digraphs having the arcs $i \rightarrow j$ and $j \rightarrow i$ at the same time. The weights $[\mathbf{T}_\alpha^{(i)}]$ must obey to the Gibbs statistics and the following relationship should be fulfilled:

$$\frac{[\mathbf{T}_\alpha^{(i)}]}{[\mathbf{T}_\alpha^{(j)}]} = \frac{g_i}{g_j} \exp \left[\frac{\mu(l_i - l_j) - (E_i - E_j)}{kT} \right]. \quad (16)$$

Here T is the temperature, μ is the electrochemical potential, g_i is the degeneracy of the i -th state with energy E_i , and l_i is the number of electrons captured by the defect.

It is possible to show that in the case of a symmetric digraph without multiple arcs there are equal numbers of trees growing into each its vertex. Thus, each vertex of a symmetric digraph with an acyclic base, i.e. consisting of an undirected tree, is a root for exactly one tree growing into it. Each vertex of a complete digraph with all pairs of vertices i and j mutually linked with each other by the counter arcs $i \rightarrow j$ and $j \rightarrow i$, is a root of M^{M-2} trees, where M is the number of the vertices. Let us examine the digraphs in Figs.1a,b,e,h with acyclic bases. In particular, base of the digraph in Fig. 1h is an undirected tree $(1-2-4-3) \& (5-2)$ and have therefore only one tree growing into each of their vertices. Fig. 3 shows the spanning trees growing into the 2nd

vertex of the digraphs of Fig. 1. Figs.3a,b,e,h show those trees growing into the vertex 2. For this reason, the stationary distribution function for these models can be constructed. For example, for bivertex digraph G [Fig. 1a]

$$F_1 = \omega_{21}/(\omega_{12} + \omega_{21}), \quad F_2 = \omega_{12}/(\omega_{12} + \omega_{21}). \quad (17)$$

Indeed, the only tree $T^{(1)} = (2 \rightarrow 1)$ of the weight $[T^{(1)}] = \omega_{21}$ grows into the vertex 1. Therefore the tree-weight of this vertex is $[1] = \omega_{21}$. Similarly, tree-weight of the vertex 2 is $[2] = [\mathbf{T}^{(2)}] = \omega_{12}$. In particular, assuming $\omega_{12} = C_p n + E_p$ and $\omega_{21} = C_p p + E_n$, one can get the common result of Shockley-Read-Hall recombination theory^{30,31}.

To get a more general result for multiple charge defects without excited states one should deal with the M-vertex digraph G shown in Fig. 1b. Vertex i of the digraph is a root of the only tree $T^{(i)} = 1 \rightarrow 2 \rightarrow \dots \rightarrow (i-1) \rightarrow i \leftarrow (i+1) \leftarrow \dots \leftarrow (M-1) \leftarrow M$ with the weight

$$[T^{(i)}] = \prod_{j=1}^{i-1} \omega_{j,j+1} \times \prod_{j=i+1}^M \omega_{j,j-1}. \quad (18)$$

If the upper limit in one of the products is smaller than the lower one, e.g., $i=1$ or $i=M$, then such a product is taken to be equal to unity. Tree-weight of the i -th vertex $[i]$ is equal to the weight of the tree $[T^{(i)}]$. Then according to Eq. 15

$$F_i = \prod_{j=1}^{i-1} \omega_{j,j+1} \times \prod_{j=i+1}^M \omega_{j,j-1} / \sum_{k=1}^M \prod_{j=1}^{k-1} \omega_{j,j+1} \times \prod_{j=k+1}^M \omega_{j,j-1}. \quad (19)$$

If one divides the numerator and denominator of this equation by the product of probabilities of all sequential

transitions from the M^{th} state to the 1^{st} state $\prod_{j=1}^{M-1} \omega_{j+1,j}$ and introduces the notations

$$R_1 \equiv 1, \quad (20)$$

$$R_i \equiv \prod_{j=1}^{i-1} (\omega_{j,j+1} / \omega_{j+1,j}) \quad \text{at } i = 2, \dots, M, \quad (21)$$

then the equation for distribution function can be simplified and written in the form:

$$F_i = R_i / \sum_{j=1}^M R_j \quad (i = 1, \dots, M). \quad (22)$$

Note that this equation is equally valid for the degenerate and non-degenerate conditions and when the Auger recombination processes play an important role: all these features are included in the transition probabilities ω_{ij} . Now we will apply this finding to the defects with four-vertex digraph shown in Fig. 1e. By one tree grows into each vertex of the digraph and one can write the following relationships

$$\begin{cases} F_1 = \frac{\omega_{21}\omega_{32}\omega_{43}}{D}, \\ F_2 = \frac{\omega_{12}\omega_{32}\omega_{43}}{D}, \\ F_3 = \frac{\omega_{12}\omega_{23}\omega_{43}}{D}, \\ F_4 = \frac{\omega_{12}\omega_{23}\omega_{34}}{D}, \end{cases} \quad (23)$$

where the denominator D is the sum of the numerators of

these four expressions of the system of Eq. (23). Here we will apply the finding for the defect with five states, which possesses the five-vertex digraph. In this example also only one tree grows into each vertex of the digraph in Fig. 1h and one can write down the following simple expressions for components of the distribution function:

$$\begin{cases} F_1 = \frac{\omega_{21}\omega_{34}\omega_{42}\omega_{52}}{D}, \\ F_2 = \frac{\omega_{12}\omega_{34}\omega_{42}\omega_{52}}{D}, \\ F_3 = \frac{\omega_{12}\omega_{24}\omega_{43}\omega_{52}}{D}, \\ F_4 = \frac{\omega_{12}\omega_{24}\omega_{34}\omega_{52}}{D}, \\ F_5 = \frac{\omega_{12}\omega_{25}\omega_{34}\omega_{42}}{D}. \end{cases} \quad (24)$$

Here D is the sum of the numerators of the expressions for all components of F_i as in the other examples. Based on these expressions it is possible to restore the trees, which contributes to the weights of the vertices. Distinct from the above digraphs with acyclic base, each digraph in Figs. 1c,f,g has one cycle in their bases: the digraph in Fig. 1c contains 3-vertex cycle $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ and those in Figs. 1f,g have 4-vertex cycles $1 \rightarrow 2 \rightarrow 4 \rightarrow 3 \rightarrow 1$ and $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$, respectively. The digraph in Fig. 1d has three cycles: two 3-vertex cycles $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ and $2 \rightarrow 3 \rightarrow 4 \rightarrow 2$, and one 4-vertex cycle $1 \rightarrow 2 \rightarrow 4 \rightarrow 3 \rightarrow 1$. It is possible to show that in a strong symmetric digraph with one n -vertex cycle in its base and without multiple arcs exactly n trees grow into each of its vertexes. To have two cycles of length n_1 and n_2 there are $n_1 \times n_2$ trees growing into each vertex. If there are three non-intersected cycles (without common edges) of length n_1 , n_2 and n_3 , one might expect $n_1 \times n_2 \times n_3$ trees. If these cycles are intersected [Fig. 1d], then each vertex is a root for $[(n_1 + n_2 + n_3)^2 - 2(n_1^2 + n_2^2 + n_3^2)]/4$ trees. Therefore, three, four and eight trees grow into each vertex of the digraph in Fig. 1c,f,g, and d, respectively. Having constructed all the trees for a digraph one can write down the equation for the distribution function. For example, in Fig. 3 four covering trees $T_{1 \dots 4}^{(2)}$ grow into the 2nd vertex of the digraph G [Fig. 1g]. The trees have the following weights: $[T_1^{(2)}] = \omega_{12}\omega_{32}\omega_{43}$, $[T_2^{(2)}] = \omega_{14}\omega_{43}\omega_{32}$, $[T_3^{(2)}] = \omega_{41}\omega_{12}\omega_{32}$, $[T_4^{(2)}] = \omega_{34}\omega_{41}\omega_{12}$. Hence, the tree-weight of the 2nd vertex is $[2] = \omega_{12}\omega_{32}\omega_{43} + \omega_{14}\omega_{43}\omega_{32} + \omega_{41}\omega_{12}\omega_{32} + \omega_{34}\omega_{41}\omega_{12}$. Tree-weights of the other vertices are:

$$[1] = \omega_{43}\omega_{32}\omega_{21} + \omega_{23}\omega_{34}\omega_{41} + \omega_{32}\omega_{21}\omega_{41} + \omega_{34}\omega_{41}\omega_{21},$$

$$[3] = \omega_{12}\omega_{23}\omega_{43} + \omega_{14}\omega_{43}\omega_{23} + \omega_{41}\omega_{12}\omega_{23} + \omega_{21}\omega_{14}\omega_{43}, \text{ and } [4] = \omega_{12}\omega_{23}\omega_{34} + \omega_{14}\omega_{23}\omega_{34} + \omega_{32}\omega_{21}\omega_{14} + \omega_{21}\omega_{14}\omega_{34}.$$

According to Eqs. (14) and (15) the distribution function is:

$$\begin{cases} F_1 = \frac{\omega_{43}\omega_{32}\omega_{21} + \omega_{23}\omega_{34}\omega_{41} + \omega_{32}\omega_{21}\omega_{41} + \omega_{34}\omega_{41}\omega_{21}}{D}, \\ F_2 = \frac{\omega_{12}\omega_{32}\omega_{43} + \omega_{14}\omega_{43}\omega_{32} + \omega_{41}\omega_{12}\omega_{32} + \omega_{34}\omega_{41}\omega_{12}}{D}, \\ F_3 = \frac{\omega_{12}\omega_{23}\omega_{43} + \omega_{14}\omega_{43}\omega_{23} + \omega_{41}\omega_{12}\omega_{23} + \omega_{21}\omega_{14}\omega_{43}}{D}, \\ F_4 = \frac{\omega_{12}\omega_{23}\omega_{34} + \omega_{14}\omega_{23}\omega_{34} + \omega_{32}\omega_{21}\omega_{14} + \omega_{21}\omega_{14}\omega_{34}}{D}. \end{cases} \quad (25)$$

Note that finding the expressions for the distribution function and the rate of GR processes through bistable defects using the digraph of states was carried out in Ref. ²⁶.

Upon constructing the distribution function the following

information might be helpful: if two states i and j are connected by the transitions $i \rightarrow j$ and $j \rightarrow i$ and if the transitions are the only paths linking the states, then the rates of transitions between the two states will be balanced not only in equilibrium but also in non-equilibrium stationary state: $F_i \omega_{ij} = F_j \omega_{ji}$. Arcs corresponding to the transitions are known as bridges in the digraph G : removal of these arcs will cause splitting of the digraph G into two disconnected fragments. One can easily prove it if notes that when there is

only one path $i \leftrightarrow j$ between the vertices i and j . Then any tree growing into the vertex i can be obtained from some tree growing into the vertex j by reorientation of the arc $i \rightarrow j$ into $j \rightarrow i$ and vice versa. Hence, weights of these vertices satisfy the Eq. $[i] = [j] \times \omega_{ji} / \omega_{ij}$. Then applying the Eq. (15) one obtains proof of the above statement. Due to this fact 'the principle of non-equilibrium detailed balance' will be fulfilled for any states of a system in steady state described by symmetric strong digraph with an acyclic base (see, e.g., Figs. 1a,b,e,h).

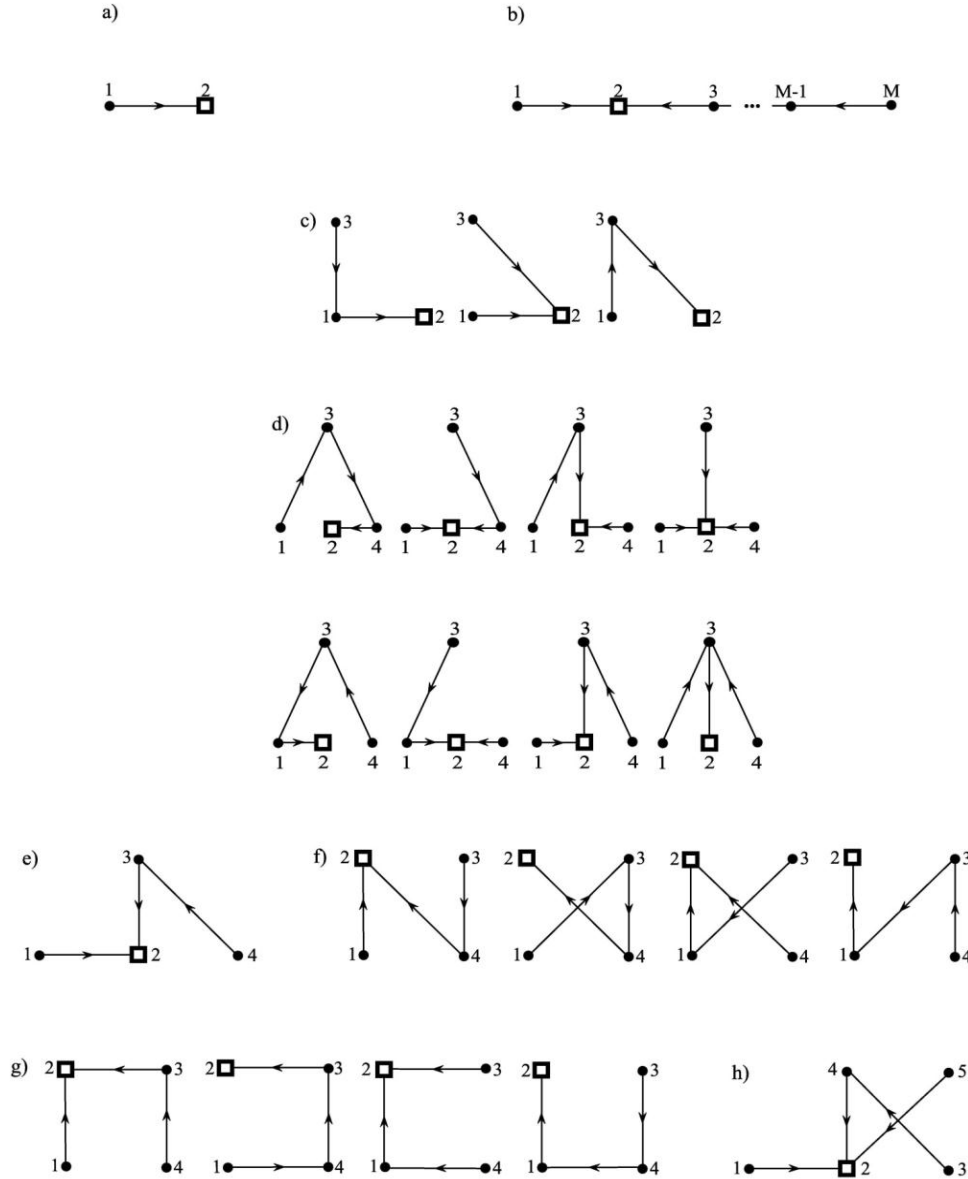


Figure 3. Spanning trees growing into the 2nd vertex of the digraphs in Figure 1: for defects with (a) two-charge and (b) M-charge without excited states, (c) two-charge defect with one excited state, (d) donor-acceptor pairs with three different charge states, (e) three-charge defects with one excited state, (f) two-charge defect with two excited states, (g) two-charge bistable defect and (h) three-charge U^- -centers (four covering trees $T_{1...4}^{(2)}$ grow into the 2nd vertex. The root vertex 2 is denoted as a square. Each of the trees makes a contribution to the tree-weight of the 2nd vertex of the digraphs

Also, it is important to note that upon constructing the distribution function loops are not taken into account, since the transitions corresponding to loops do not take the defects out of their states. Presence of loops means that the defect has influences on the rate of electronic transitions through a defect without changing its charge state. Hence, one might think that the loops have no effect on the distribution function. Possible mechanisms of such static influence are discussed in the Section II.

3.3. Graph Theory in Simplifications of the Scheme of Electronic Transitions of Small Probability. Analysis of Digraph of States for Defects at High Injection Levels

In the analysis of electrical properties of a semiconductor it is interesting to know concentration of the center of recombination in each of its states in asymptotic level, e.g., at high injection levels, temperatures, electric field, etc. Such analysis requires some simplifications in electronic transitions in the model of the defect. The simplification itself can become a challenge when the defect can be in several configurations and charge states. In kinetic theory simplification is based on neglecting the defect transitions of smallest probability. Below we describe how the graph theory can help to solve the challenge. As discussed above, the stationary distribution function F_i should be constructed using the digraph of states G , which is designed by searching for all the rooted covering trees. If the defect possesses many states and complicated scheme of allowed transitions searching for the trees might be complicated. For example, number of covering rooted trees for a complete digraph with only five vertices is equal to 625, since 5^{5-2} trees grow into each vertex. Manual operation with such number of trees is a time consuming work, which can be done using a computer. Here one can use one of the searching algorithms (see, e.g., Ref.[3]). First, the advantage of the search algorithm of all undirected spanning trees should be taken into account³. Edges of the trees will be assigned such an orientation, so that they will be turned into the directed trees growing into the wished vertex. It is convenient to start the orientation from the edges incident to the vertex selected as the root: they must be assigned the directions which lead to the root vertex, then the edges incident to the directed arcs should be oriented in such a manner that they lead to the beginning of already directed arcs, and so on until all edges will get their orientation. Note that for a symmetric digraph without multiple arcs each of its spanning trees generates by exactly one tree growing into each vertex.

Of course, one can try to simplify such a complicated system, because, in practice, contribution from the trees to the weights of the vertices will differ each from other. Only a few trees of maximum weight might play primary role in the weight of each vertex of a digraph, whereas contribution from the others can be ignored. In such cases it is possible to limit ourselves by finding only those trees with maximum weight. It can be done by taking the advantage of any

algorithm, specifically created for this purpose, e.g., the algorithm developed by J. Edmonds⁴. However if we are interested in asymptotic limit of distribution function upon increase of the excitation level, then it is advisable to follow the above way because behaviour of a system far from an equilibrium is actually determined only by maximal trees.

Indeed, probabilities of transitions of defects ω_{ij} depend on free carrier densities, temperature, and intensity of incident illumination, external electric field, and other parameters according to power and/or exponential dependencies. Weights of the trees, being multiplication of the probabilities ω_{ij} , will also depend on the same parameters. Because of this, upon influence of external excitations, some of the above-mentioned parameters might start to deviate from the equilibrium value leading to gradual separation of the trees growing into a vertex according to their weights. However, the increase of the external influence can change only weight of the oriented trees, but not their composition. So, it might happen that contribution from one or more trees rooted to a given vertex, with the maximum weights of the same magnitude achieved at the asymptotic limit, might become much larger than that from the other trees of smaller weight growing into the same oriented trees. Since properties of the system is determined by maximal trees, this feature allows consideration of only maximal trees growing into each vertex, when the external excitation of the system already caused sharp gradual separation of the trees with respect to their weights.

This way of simplification of analyses of complicated models, which takes into account all leading trees, allows one to avoid the danger of oversimplification, when the model might lose some of its important features. Suppose we have simplified a model of a defect with a complicated scheme of allowed transitions by neglecting some transitions because of their small probability. However, before doing it we should know the role of the transition in the scheme. Although probability of a transition is smaller than the others, it might be located in strategically important place of the scheme of transitions. Properties of the defect with this particular small weight transition and without it might differ each from other. At this point it is worth to note that stationary state of a system is formed at cooperative action of all transitions of the defect, including the very weak ones, e.g., those that are responsible for long-term relaxation of optical and thermal excitations.

The following model illustrates the above discussion. Let us consider the model of a defect described by the digraph in Fig. 1g with the weights of its arcs, which depend on some parameter n as follows: $\omega_{41} = n, \omega_{14} = 1, \omega_{23} = 10n, \omega_{32} = 1, \omega_{12} = \omega_{21} = 0.01$ and $\omega_{34} = \omega_{43} = 1$. Distribution function for the system is described by Eq. (25). Substituting the probabilities ω_{ij} into Eq.(25) one can find that $F_3 = [3]/D = (0.1n^2 + 10.1n + 0.01)/(10.1n^2 + 21.24n + 1.05)$, i.e. as n increases from $n \approx 0.33$, F_3 monotonically decreases asymptotically to 0.01. Let us now notice that at $n \geq 1$, probabilities of the transitions $1 \leftrightarrow 2$ ω_{12} and ω_{21} are at least two orders of magnitude smaller than those of all other

transitions and the difference further increases with increasing n . It might give the impression that these two transitions characterized by ω_{12} and ω_{21} should not influence strongly on stationary state of a system at any magnitudes of n . However, if one neglects these transitions from the scheme, then one can get a simplified digraph, which has only by one tree growing into each vertex with the following tree-weights: $[1] = \omega_{41}\omega_{34}\omega_{23} = 10n^2$, $[2] = \omega_{14}\omega_{43}\omega_{32} = 1$, $[3] = \omega_{23}\omega_{41}\omega_{43} = 10n$, $[4] = \omega_{14}\omega_{34}\omega_{23} = 10n$. As a result, $F_3 = [3]/D = 10n/(10n^2 + 20n + 1)$, which asymptotically approach zero as $F_3 \sim 1/n$. So, the accuracy for F_3 estimated by the simplified model decreases proportionally to n and the decrease is because of the incorrect simplification. This example demonstrates that care should be taken upon exclusion of the transitions $1 \leftrightarrow 2$, ω_{12} and ω_{21} with small weight. The reason is that at $n > 10^2$ the tree of the maximal weight primarily causing the tree-weight of the 3rd vertex of the initial digraph, is $(4 \rightarrow 1 \rightarrow 2 \rightarrow 3)$ with weight $\omega_{41}\omega_{12}\omega_{23} = 0.1n^2$, which contains the weak transition $1 \rightarrow 2$. If one removes the weak transition from the scheme, then the leading tree growing into the vertex 3 becomes a less ponderable one and the asymptotical value of the weight of the 3rd vertex will change. Note, that similar point concerns also the 2nd vertex.

The above analysis shows that in theoretical studies of GR processes through point defects simplifications of a defect model should be based not only magnitude of the probability of some transitions, but also on the role of each of the transitions in the set of the trees. This point could be considered as advantage of the graph theory compared to the kinetic approach. Within the framework of the traditional approach based on the solution of the system of kinetic equations, one can hardly find a simple and convenient method of correct simplification of the complex models, because, as discussed above, the very essence of the problem is closely associated with analysis of objects belonging to the graph theory. The graph theory gives the exclusive possibilities of solution of the challenge, because the search algorithms of maximal trees are rather simple and do not require preliminary simplification of models.

Below we will use these ideas for analysis of the digraph G in Fig. 4 for bipolar high injection levels. Fig. 4a shows the defect with two-charge states with a ground state 1 and two excited states 3 and 5 corresponding to the empty defect, and a ground state 2 and excited state 4 corresponding to the defect with one trapped electron. Suppose that the probabilities of intra-center transitions ω_{13} , ω_{31} , ω_{35} , ω_{53} , ω_{24} and ω_{42} do not depend on free carrier densities. In the asymptotical limit the transition $3 \rightarrow 2$ is determined by capture of electrons to the defect level from the conduction band: $\omega_{32} = C_n^{32} n$, the reverse transition $2 \rightarrow 3$ is determined by capture of holes from the valence band: $\omega_{23} = C_p^{23} p$. The transition $3 \rightarrow 4$ corresponds to capture of an electron from the valence band: $\omega_{34} = E_p^{34}$, and $4 \rightarrow 3$ corresponds to capture of a hole: $\omega_{43} = C_p^{43} p$. The transition $5 \rightarrow 4$ is

capture of an electron from the conduction band by Auger mechanism, when one more free electron participates in the process: $\omega_{54} = T_{nn}^{54} n^2$, and the transition back into the state

5 occurs due to hole capture: $\omega_{45} = C_p^{45} p$. For demonstration purposes in Fig. 4a we present degree of the power as the weights of arcs of the digraph G , which along with the free electron and hole concentrations p and n , are incorporated into the probabilities of transitions. Eight trees grow into each vertex of this digraph [Fig. 4a], so that total number of covering trees equals to 40. As mentioned in previous section, number of the trees can be found with help of the matrix K . However, we shall be interested only in the trees of largest weights in an asymptotical limit. Following a procedure for the search of the trees of maximal weight, e.g., by algorithm developed by Edmonds⁴, one can find that there are only ten such trees [Fig. 4b]. By one maximal tree grows into each of the vertices 1, 2, and 3. Summing the weights of their arcs indicated in Fig. 4b, one can find that the weight of each of the trees is proportional to the 4th degree of the parameter of external excitation. Three maximal trees grow into the vertex 4 with weights proportional to the 3rd degree of the excitation parameter. Four maximal trees grow into the vertex 5 with weights proportional to the 2nd degree of the parameter of excitation. Therefore, in an asymptotical limit one can get:

$$\begin{aligned}
 [1] &= \omega_{31}\omega_{23}\omega_{43}\omega_{54} = \omega_{31}C_p^{23}C_p^{43}T_{nn}^{54}p^2n^2, [2] = \omega_{13}\omega_{32}\omega_{43}\omega_{54} = \\
 &\omega_{13}C_n^{32}C_p^{43}T_{nn}^{54}pn^3, [3] = \omega_{13}\omega_{23}\omega_{43}\omega_{54} = \omega_{13}C_p^{23}C_p^{43}T_{nn}^{54}p^2n^2, \\
 [4] &= \omega_{13}\omega_{54}(\omega_{23}\omega_{35} + \omega_{32}\omega_{24} + \omega_{23}\omega_{34}) = \omega_{13}T_{nn}^{54}n^2 (C_p^{23}p\omega_{35} + \\
 &C_n^{32}n\omega_{24} + C_p^{23}pE_p^{34}), [5] = \omega_{13}(\omega_{23}\omega_{43}\omega_{35} + \omega_{23}\omega_{34}\omega_{45} + \\
 &\omega_{32}\omega_{24}\omega_{45} + \omega_{23}\omega_{45}\omega_{35}) = \omega_{13}p (C_p^{23}C_p^{43}p\omega_{35} + C_p^{23}E_p^{34} \\
 &C_p^{45}p + C_p^{45}C_n^{32}n\omega_{24} + C_p^{23}C_p^{45}p\omega_{35}). \text{ If the electro-} \\
 &\text{neutrality condition } p \approx n \text{ is fulfilled, then the distribution} \\
 &\text{function will depend on carrier density as follows: } F = \\
 &\{\varphi_1, \varphi_2, \varphi_3, \varphi_4/n, \varphi_5/n^2\}, \text{ where } \varphi_1 = \omega_{31}C_p^{23}C_p^{43}T_{nn}^{54}/D, \\
 &\varphi_2 = \omega_{13}C_n^{32}C_p^{43}T_{nn}^{54}/D, \varphi_3 = \omega_{13}C_p^{23}C_p^{43}T_{nn}^{54}/D, \varphi_4 = \omega_{13} \\
 &T_{nn}^{54}(C_p^{23}\omega_{35} + C_n^{32}\omega_{24} + C_p^{23}E_p^{34})/D, \varphi_5 = (C_p^{23}C_p^{43}\omega_{35} + \\
 &C_p^{23}E_p^{34}C_p^{45} + C_n^{32}\omega_{24}C_p^{45} + C_p^{23}C_p^{45}\omega_{35})/D \text{ with the} \\
 &\text{denominator } D = C_p^{43}T_{nn}^{54}(\omega_{31}C_p^{23} + \omega_{13}C_n^{32} + \omega_{13}C_p^{23}).
 \end{aligned}$$

Analysis shows that upon increase of the injection level, occupation of the states 4 and 5 approaches zero inverse proportionally to n and n^2 , respectively. However, portions of defects in the states 1, 2 and 3 are stabilized on φ_1 , φ_2 and φ_3 , accordingly. Incidentally we shall note that the transitions $4 \rightarrow 2$ and $5 \rightarrow 3$ are included in none of the maximal trees [Fig. 4b]. Therefore their elimination from the model does not affect noticeably on the asymptotic limit of the distribution function. All the other transitions are used by the maximal trees. Therefore, even if probabilities of some of the transitions will be considerably smaller than ω_{12} and ω_{53} , elimination of any of them may disturb the distribution function seriously. Thus, only after construction of maximal

trees one can know whether influence of a transition on distribution function of the defects can be neglected or not.

By using the distribution function one can find the rate of GR transitions. In the above example asymptotic limit of the rate of intra-center spontaneous transitions $3 \rightarrow 1$, $4 \rightarrow 2$ and $5 \rightarrow 3$ will be equal to $R_{31} = N_{\text{tot}} \phi_3 \omega_{31}$, $R_{42} = N_{\text{tot}} \phi_4 \omega_{42}/n$ and $R_{53} = N_{\text{tot}} \phi_5 \omega_{53}/n^2$. If any of these transitions are irradiative, then the rate of emission either saturates for the transition $3 \rightarrow 1$, or decreases inverse proportionally to n for $4 \rightarrow 2$ and to n^2 for $5 \rightarrow 3$. Section II of this paper discusses the technique of finding the stationary rate of GR transitions with help of the digraph of states.

3.4. Specular Features of the Models Described by Weakly Connected Digraphs

So far we have considered the case when the digraph of states $\mathbf{G}$ is covered by the “growing into” type of trees. Namely in such case the distribution function can be found by the tree-weight rule described by Eqs.(12)-(15). Connected symmetric digraphs, strong digraphs, which are not necessarily to be symmetric, and the above mentioned examples described by symmetric digraphs possess the specific feature. A wider class of digraphs that has only one strongly connected component of sink-type, denoted further as the $\mathbf{A}$ -component, can also possess such a feature. Types of connectivity components are discussed in Appendix A. In this case all the vertices of the $\mathbf{A}$ -component (to be called hereafter as $\mathbf{A}$ -vertices and designated by i_A) will be reachable from any vertex of the digraph $\mathbf{G}$. Namely, all of them will be accessible mutually and also accessible from the other vertices which do not belong to the $\mathbf{A}$ -component (to be denoted by $\overline{\mathbf{A}}$ -vertices). They all will belong to the source and transit components. Because of this reason each $\mathbf{A}$ -vertex will be a root for at least one spanning tree and will, therefore, have a non-zero tree-weight. On the contrary, $\overline{\mathbf{A}}$ -vertices, being inaccessible from $\mathbf{A}$ -vertices, cannot be roots for spanning trees and, hence, their weights equal to zero. It is evident that at any initial distribution of defects on their states, occupation of the $\overline{\mathbf{A}}$ -states can steadily decrease, because probability of transition of the defects into the $\overline{\mathbf{A}}$ -states is equal to zero, while that going out from these states is not zero. So, more and more defects will gradually be accumulated in the $\mathbf{A}$ -states, since they are incapable of leaving the states into $\overline{\mathbf{A}}$ -vertices. In steady state conditions all the defects will occupy only $\mathbf{A}$ -states, whereas the $\overline{\mathbf{A}}$ -states will become completely unoccupied and transitions linking them with each other or with the $\mathbf{A}$ -states will be completely stopped. In view of ‘dying away’ of the

$\overline{\mathbf{A}}$ -states during relaxation of the system into the steady state, at calculation of the stationary distribution function one can consider only the $\mathbf{A}$ -states and transitions, linking them. Then instead of the Eq. (15) one can use the following equation for the $\mathbf{A}$ - and $\overline{\mathbf{A}}$ -states, respectively.

$$F_{i_A} = [i_A]' / [\mathbf{A}]' \quad (26)$$

$$F_{\overline{i_A}} = 0 \quad (27)$$

Tree-weights of the $\mathbf{A}$ -vertices can be found by summing the weights of the oriented trees, which are cores for the $\mathbf{A}$ -component (marked by a stroke in the weights $[i_A]'$) and not for the whole digraph $\mathbf{G}$. Weight of the whole $\mathbf{A}$ -component in the denominator of the Eq.(26) is the sum of the tree-weights of all vertices included into it:

$$[\mathbf{A}]' \equiv \sum_{i_A} [i_A]'. \quad (28)$$

If the digraph $\mathbf{G}$ is strong, i.e. if it consists of only the $\mathbf{A}$ -component, then the Eqs.(26)-(28) turn into the initial Eqs.(14) and (15). As an example we shall consider the eleven-vertex digraph $\mathbf{G}$ [Fig. 5]. Analysis shows condensation $\mathbf{G}^*$ of the digraph $\mathbf{G}$, which is a good way to show the relationships between the strongly connected components of $\mathbf{G}$ (see, e.g., Ref.³). It is seen in the Fig. 5b that $\mathbf{G}$ contains four strong components: one source component $\mathbf{R} = \{1,2,6\}$, two transit components $T_1 = \{7,10,11\}$ and $T_2 = \{7\}$, and one sink component $\mathbf{A} = \{3,4,5,9\}$. Weights of the states not included into the $\mathbf{A}$ -component are equal to zero. It means that at the steady state conditions all the defects will be in the states 3, 4, 5, and 9. To calculate the tree-weights of the states one should sum up the weights of the trees covering the $\mathbf{A}$ -component [Fig. 5c]: $[3]' = [\mathbf{T}_1^{(3)}]' = \omega_{5,4} \omega_{9,4} \omega_{4,3}$, $[4]' = [\mathbf{T}_1^{(4)}]' + [\mathbf{T}_2^{(4)}]' = \omega_{5,4} \omega_{9,4} \omega_{3,4} + \omega_{5,4} \omega_{3,9} \omega_{9,4}$, $[5]' = [\mathbf{T}_1^{(5)}]' + [\mathbf{T}_2^{(5)}]' = \omega_{3,4} \omega_{9,4} \omega_{4,5} + \omega_{3,9} \omega_{9,4} \omega_{4,5}$, $[9]' = [\mathbf{T}_1^{(9)}]' = \omega_{5,4} \omega_{4,3} \omega_{3,9}$. According to the tree-weight rule [Eqs. (26)-(28)], the stationary distribution functions will be $F_3 = \omega_{5,4} \omega_{9,4} \omega_{4,3} / D$, $F_4 = \omega_{5,4} \omega_{9,4} (\omega_{3,4} + \omega_{3,9}) / D$, $F_5 = \omega_{4,5} \omega_{9,4} (\omega_{3,4} + \omega_{3,9}) / D$, $F_9 = \omega_{5,4} \omega_{4,3} \omega_{3,9} / D$, $F_{1,2,6,7,8,10,11} = 0$. Here the denominator D is equal to the sum of the numerators of all the fractions. Note that, as the digraph $\mathbf{G}$ has the only $\mathbf{A}$ -component, one could also perform the calculation using the Eqs. (14) and (15), but then one had to deal with all 1368 (!) trees covering $\mathbf{G}$ and, after simplification of the fraction [Eq.(15)], one can get the same result. Therefore, the preliminary demarcation of the $\mathbf{A}$ -component in the digraph of states $\mathbf{G}$ may assist greatly in finding the distribution function F_i . This is one of the advantages of the graph theory over the other ways of deriving F_i by solving the system of equations.

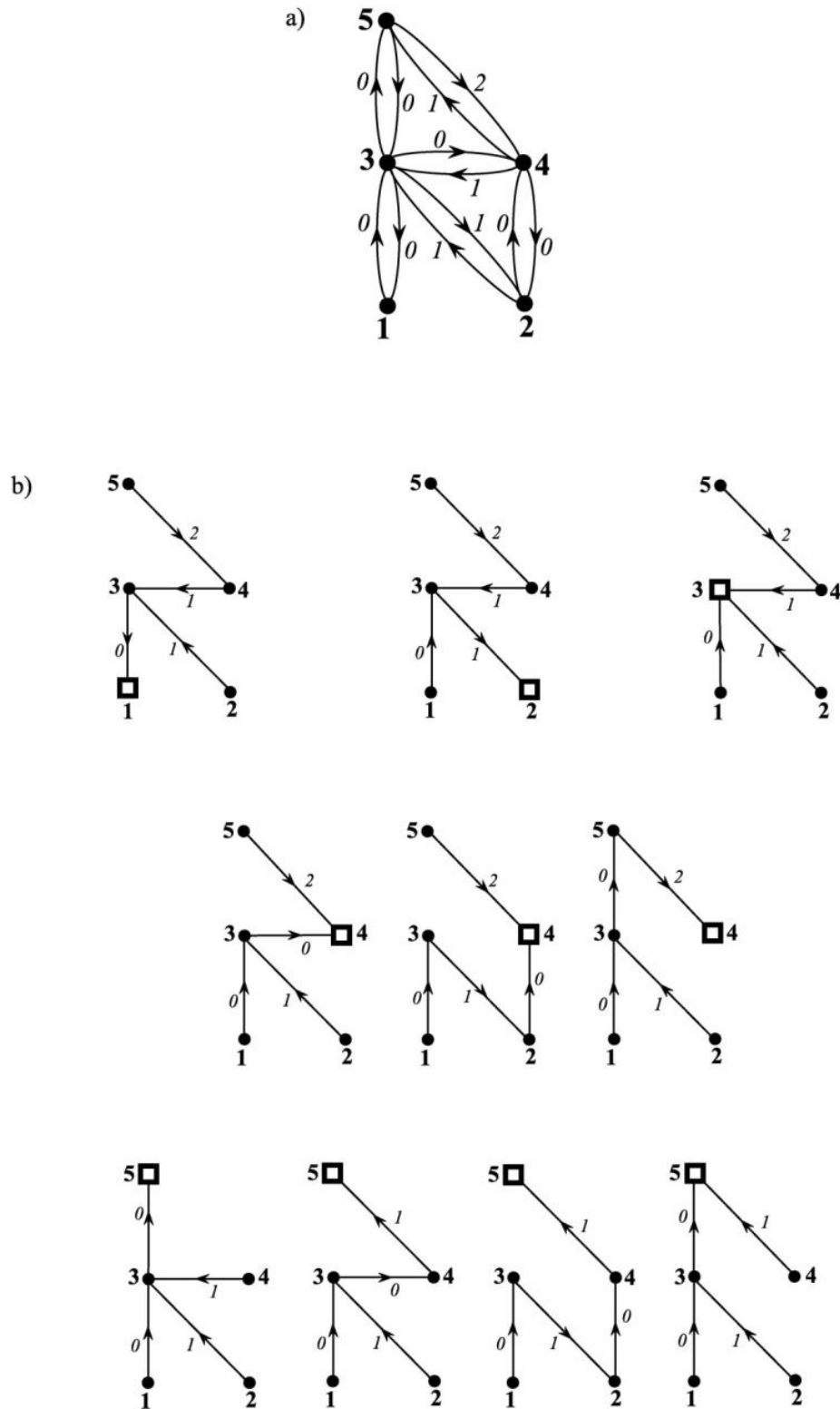


Figure 4. (a) A digraph of states for a hypothetical defect with two-charge states with a ground state 1 and two excited states 3 and 5 corresponding to the empty defect, and a ground state 2 and excited state 4 corresponding to the defect with one trapped electron. Weights of the arcs of the digraph G are shown as the degree of the power, which along with the free electron and hole concentrations p and n , are incorporated into the probabilities of transitions. Eight trees grow into each vertex of this digraph, so that total number of covering trees equals to 40. (b) The ten rooted trees with the largest weight and determining the asymptotic values of the tree-weights of all the vertices. Exponent for the weights of the trees can be calculated by summing up the indicated weights of their arcs

Let us now analyse the case, when the digraph G has several A -components and let the number of the components be m_A . Such a digraph cannot have any spanning rooted trees, since none of its vertices is accessible simultaneously from all other vertices. In particular, there is no possibility to pass from one A -component into another. Formally it means, that the tree-weight $[i]$ of each vertex calculated with the help of the trees covering the whole digraph G , should be zero and calculation of the distribution function just using the Eq. (15) becomes impossible. However, it is possible to formulate a more general tree-weight rule similar to that in Eqs. (26)-(28), which allows one to calculate the stationary distribution function for any digraph of states. First of all let us note that at steady state conditions all the defects will be only in A -states at any scheme of allowed transitions. The remaining R - and T -states [Appendix A] will be unoccupied due to irreversible outflow of the defect into the A -states during relaxation of the system into its stationary state and will thus cease to participate in the other transitions. In case of the only A -component, it was already evident that all defects will eventually occupy just this component. However, in case of several A -components portion of the defects in the A -component will depend on two points: one is the probabilities of transitions linking the different strong components, which can be time-dependent. The other one is the initial conditions, which are the initial non-stationary distribution of the defects on their states.

Let us consider, for example, a digraph G in Fig. 6a with its condensation G^* in Fig. 6b. It has five strong components: two source components $R_1 = \{1,2,6\}$ and $R_2 = \{4,7\}$, one transit component $T = \{3,4,7\}$, and two sink components $A_1 = \{4,7\}$ and $A_2 = \{9,10\}$. If initially all the defects were in the states belonging, say, to the components T and R_2 , then after the steady conditions reached, all of them, evidently, will occupy the states of the A_2 -component, i.e. in the states 9 and 10. However, if initially some part of the defects were in the R_1 -component, then upon relaxing to the stationary state some defects will be locked in the A_1 -component, i.e. the defects will stay in the 5th state, and remaining defects will be in the A_2 -component. By virtue of mutual inaccessibility between states belonging to different A -components and of the absence of direct influence of them on each other, the set of states breaks up into subsets (more precisely, into m_A), which are isolated each from other. The defects incorporated into each of the subsets will evolve according to internal regulations of the subset. By considering each subsystem corresponding to the A -component irrespective of others, we can conclude that the stationary distribution of defects within the A -component should obey to the rule described by the Eq. (26). Consequently, if the steady state is already reached and the portion of the defects incorporated into the first A -component forms η_1 , into the second A -component forms η_2 , ..., into the m_A -th component forms η_{m_A} , then the distribution function can be calculated by:

$$F_{i_{A_\mu}} = \eta_\mu \cdot \frac{[i_{A_\mu}]'}{[A_\mu]'} \quad (29)$$

for the A_μ -states ($\mu = 1, \dots, m_A$) and

$$F_i = 0 \quad (30)$$

for the states i not belonging to A -components. Portions of the defects η_μ incorporated into the component A_μ ($\mu = 1, \dots, m_A$) are determined by prehistory of reaching the stationary state and obey the natural requirement

$$\sum_{\mu=1}^{m_A} \eta_\mu = 1. \quad (31)$$

The stroke in Eq. (29) for the weights $[i_{A_\mu}]'$ shows that it is the sum of the weights of the trees covering only A_μ -component of the digraph G . Weight of the component is the sum of the weights of the vertices coming into it:

$$[A_\mu]' = \sum_{i_{A_\mu}} [i_{A_\mu}]' \quad (\mu = 1, \dots, m_A). \quad (32)$$

This is the tree-weight rule in its most general form. It allows to calculate the stationary distribution function of defects with any scheme of allowed transitions. However, only symmetrical digraphs can correctly describe the system in the state at the equilibrium or near to the thermodynamic equilibrium, when the direct and reverse transitions play equally important role in the balance of flows of probability. The tree-weight rule for such models can be described by Eqs. (12)-(15). Non-symmetric models can be used for description of only highly excited systems, and if the digraph of states has several A -components, then it is necessary to use the common rule described by Eqs. (29)-(32). However, if there is only one A -component then one can use Eqs. (26)-(28), which takes the form of Eqs. (12)-(15) for a strong digraph G .

For application of Eqs. (29)-(32), we shall analyse the digraph in Fig. 6a. It has two A -components. The tree-weight of the only vertex in A_1 is: $[5]' = [T_1^{\mathcal{Q}}]' \equiv 1$. By definition weight of a trivial tree consisting of only one vertex, is equal to unity. Tree-weights of both vertices in A_2 are: $[9]' = [T_1^{\mathcal{Q}}]' = \omega_{10,9}$ and $[10]' = [T_1^{\mathcal{Q}}]' = \omega_{9,10}$. If as a result of the transient processes the portion of the defects in A_1 equals to η_1 , then their portion η_2 in A_2 will be equal to $(1 - \eta_1)$ and the defects will populate their states as follows: $F_5 = \eta_1$, $F_9 = (1 - \eta_1) \cdot \frac{\omega_{10,9}}{\omega_{9,10} + \omega_{10,9}}$, $F_{10} = (1 - \eta_1) \cdot \frac{\omega_{9,10}}{\omega_{9,10} + \omega_{10,9}}$, $F_{1-4,6-8} = 0$. Again, as in the previous example, we have managed to obtain the distribution function easily due to the possibility of dealing only with the A -components of the digraph G .

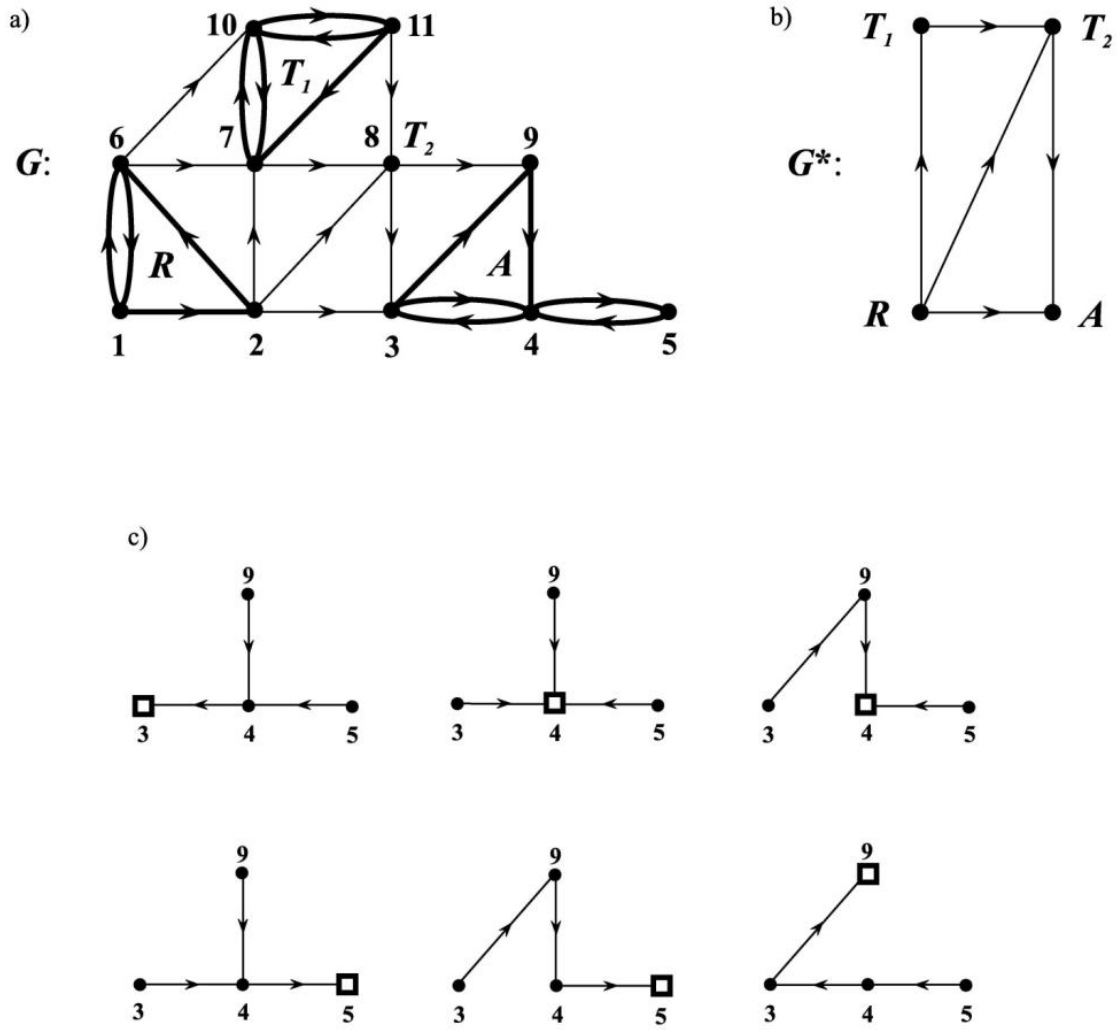


Figure 5. (a) Weak digraph G with one source component $R = \{1, 2, 6\}$, two transit components $T_1 = \{7, 10, 11\}$ and $T_2 = \{8\}$ and one sink component $A = \{3, 4, 5, 9\}$. For visualization the strong components are depicted by bold lines. (b) Condensation of the digraph G^* schematically illustrates the connections between the components. The step-by-step outflow of defects from R - and $T_{1,2}$ -states results in occupation of only the A -states 3, 4, 5, 9 by the defects at steady state conditions. (c) The tree-weight of each vertex belonging to the A -component is determined by the trees covering the component

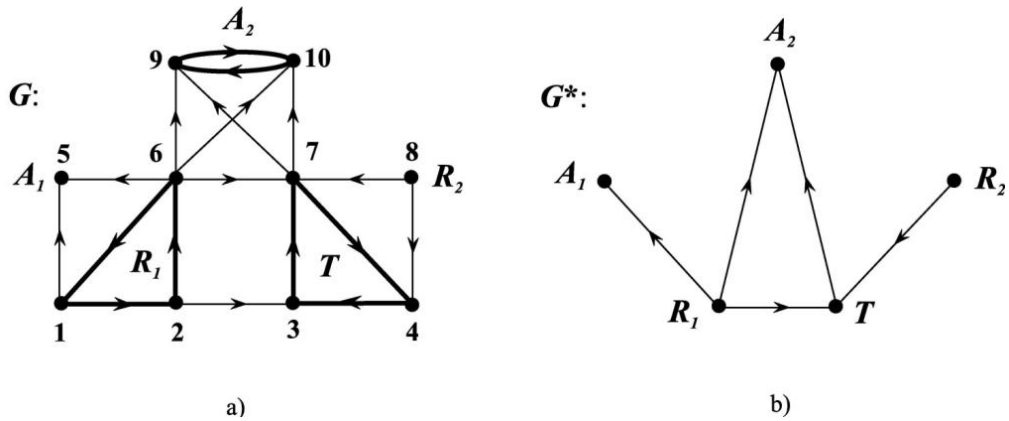


Figure 6. (a) Weak digraph G with two source components $R_1 = \{1, 2, 6\}$ and $R_2 = \{4, 7\}$, one transit component $T = \{3, 4, 7\}$ and two sink components $A_1 = \{5\}$ and $A_2 = \{9, 10\}$. (b) Links between the components. In stationary conditions all defects will be only in A -states. Although the distribution of defects between the components A_1 and A_2 will depend on previous history of reaching the steady state conditions, distribution of defects on states within each of the A -component is determined by only the tree-weights of the vertices of the corresponding A -component

Analysis of the general rule described by Eqs. (29)-(32) shows that the tree-weights $[i_{A_\mu}]'$ determine the relative populations of the states only within the A_μ -components and are independent of how the system approaches the stationary state. Therefore, for finding the normalized distribution function for $m_A \geq 2$ one needs to know η_μ ($\mu = 1, \dots, m_A$) for m_A connected with Eq. (17) and determining the portions of defects from their total number being in each of the A_μ -components. This is the relation between the rank of the system of algebraic Eqs. (3) and (4) and one of the numerical characteristics of the digraph G , which is the number of its strong components m_A of sink type:

$$\text{rank} \mathbf{W} = M - m_A. \quad (33)$$

Here $\mathbf{W}$ is the $M \times M$ -matrix of the coefficients [Appendix A] of the system of Eq. (2).

4. Generation-recombination Processes

4.1. Digraph of States and the Rate of Generation-recombination Transitions

4.1.1. Some Quantities Describing the GR-transitions

As a rule, transition of a defect from one state into another can occur by different channels, characterized by probability and change of the number of free carriers in each of the allowed bands. Transition probability of a defect from the state i into the state j by the particular channel α ($i \rightarrow j$) will be denoted by $\omega_{ij}^{(\alpha)}$. Change of number of the free electrons and holes caused by the transition will be denoted by $\nu_{ij}^{(\alpha)}$ and $\pi_{ij}^{(\alpha)}$, respectively. For example, for transitions in Fig. 7, $\nu_{ij}^{(a,d,e,f)} = -1$ [Fig. 7 a, d, e, and f], $\nu_{ij}^{(b,c)} = 0$ [Fig. 7, b and c], $\pi_{ij}^{(a)} = 0$ [Fig. 7, a], $\pi_{ij}^{(b,c,e,f)} = -1$ [Fig. 7, b, c, e, and f], $\pi_{ij}^{(d)} = +1$ [Fig. 7, d]. The net transition probability ω_j of a defect $i \rightarrow j$ is equal to the sum of the probabilities of transitions by all possible channels:

$$\omega_j = \sum_{\alpha} \omega_{ij}^{(\alpha)}. \quad (34)$$

If a defect will perform many transitions from the state i into the state j , then the ratio $\omega_{ij}^{(\alpha)} / \omega_j$ will give the portion of the transition occurring by the particular mechanism α . Since at each such transition of a defect $i \rightarrow j$ number of free carriers in their “native” bands varies by $\nu_{ij}^{(\alpha)}$ and $\pi_{ij}^{(\alpha)}$, then the number of electrons in the conduction and valence bands changes on average by

$$\nu_{ij} = \sum_{\alpha} \omega_{ij}^{(\alpha)} \nu_{ij}^{(\alpha)} / \omega_j, \quad (35)$$

$$\pi_{ij} = \sum_{\alpha} \omega_{ij}^{(\alpha)} \pi_{ij}^{(\alpha)} / \omega_j, \quad (36)$$

respectively. Note that distinct from the integer quantities $\nu_{ij}^{(\alpha)}$ and $\pi_{ij}^{(\alpha)}$ characterizing separate mechanisms, the quantities ν_{ij} and π_{ij} averaged over all the mechanisms will be non-integer. Let, for example, transition of an acceptor from the zero-charge state “0” into the negatively charged state “1” can occur by one of the three ways: (i) by capturing an electron from the conduction band by the multi-phonon mechanism of energy dissipation. We shall denote this channel by “a”. It is characterized by the probability $\omega_{01}^{(a)} = C_n^{01} n$, by $\nu_{01}^{(a)} = -1$ and $\pi_{01}^{(a)} = 0$. (ii) By the Auger mechanism with transmission of some energy to another free electron (termed as the channel “b”: $\omega_{01}^{(b)} = T_{nn}^{01} n^2$, $\nu_{01}^{(b)} = -1$ and $\pi_{01}^{(b)} = 0$). (iii) By capturing an electron from the valence band termed as the channel “c”, described by the probability of generation of a hole $\omega_{01}^{(c)}$ and changes of the number of carriers by $\nu_{01}^{(c)} = 0$ and $\pi_{01}^{(c)} = +1$. Then according to Eqs. (34)-(36) each transition $0 \rightarrow 1$ is accompanied by changes of the number of free electrons and holes $\nu_{01} = -\lambda_{01} / (1 + \lambda_{01})$ and $\pi_{01} = 1 / (1 + \lambda_{01})$, respectively. Here $\lambda_{01} = (\omega_{01}^{(a)} + \omega_{01}^{(b)}) / \omega_{01}^{(c)}$. In the limit $\lambda_{01} \gg 1$, which means that the transition probability by the channel “c” is much smaller than that by the channels “a” and “b”, or, on the contrary, at $\lambda_{01} \ll 1$, when the channel “c” is dominating, the magnitudes of ν_{01} and π_{01} will practically be coincident with those of $\nu_{01}^{(\alpha)}$ and $\pi_{01}^{(\alpha)}$ corresponding to the dominating channel.

Further, any transition $i \rightarrow j$ is characterized by change of the number of electrons bound on a defect $\Delta I_j = I_j - I_i$, where I_i is the number of electrons on the defect in the i -th state. It is evident that ΔI_j is independent of the mechanism of the transition α , and it depends only on the initial i and final j states of the defect. Based on the fact that at any GR-transitions total number of carriers remains constant and the transitions only redistribute the carriers between the allowed bands and the defect one can write that

$$\Delta I_j + \nu_{ij}^{(\alpha)} = \pi_{ij}^{(\alpha)}. \quad (37)$$

Similar equality holds also for the quantities averaged over all channels:

$$\Delta I_j + \nu_{ij} = \pi_{ij}. \quad (38)$$

To prove validity of the Eq. (38), one should multiply both sides of Eq. (37) by the transition probability of the channel α $\omega_{ij}^{(\alpha)}$, then sum them up over all channels and divide them by the total transition probability ω_j . Then, using the Eqs. (35) and (36) and accounting for the fact that ΔI_j is the same for all channels, one can get the Eq. (38).

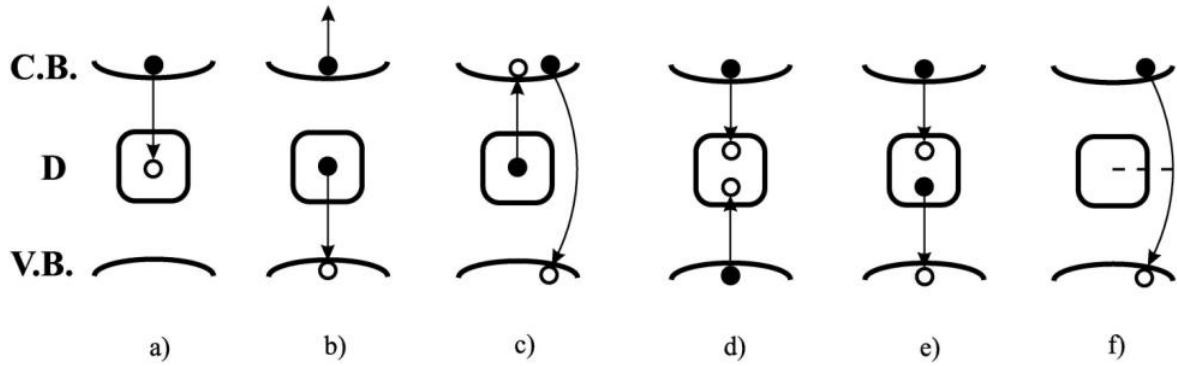


Figure 7. Scripts of some transitions between the defect “D” levels and conduction/valece bands. The conduction and valence bands are marked as “C.B.” and “V.B.” respectively, and an electron and a hole are figured accordingly as the closed and open circles. (a) Capture of a conduction band electron by a defect, (b) recombination of an electron trapped on the defect with a valence band hole with transmission of some energy liberated to a free electron, (c) band-to-band recombination of an electron-hole pair with some part of energy spent for excitation of an electron from the defect to the conduction band, (d) simultaneous capture of one electron from the conduction band and another one from the valence band, (e) and (f) transitions consisting of simultaneous capture of a conduction band electron and a valence band hole (e) on the defect and (f) around the defect, that does not change number of electrons on the defect and, therefore, keeps its charge unchanged. Such a defect can nevertheless pass through the other quantum states

4.1.2. Rate of GR-transitions at Steady State

The rate $R_{ij}^{(\alpha)}$ of the transitions of defects $i \rightarrow j$ per unit volume is equal to product of density N_i of the defects in the i -th initial state by the probability of the transitions $\omega_{ij}^{(\alpha)}$, i.e. $R_{ij}^{(\alpha)} = N_i \times \omega_{ij}^{(\alpha)}$. Total rate R_{ij} of transitions of defects $i \rightarrow j$, being the sum of all particular rates $R_{ij}^{(\alpha)}$, is equal to product of the defect density N_i by total probability of the transition ω_{ij} : i.e. $R_{ij} = \sum_{\alpha} R_{ij}^{(\alpha)} = N_i \times \omega_{ij}$. Since each transition $i \rightarrow j$ of the defect changes the number of free electrons on average by ν_{ij} and that of holes by π_{ij} , then one can find the equation for the net rate of change of the number of free electrons U_n and holes U_p due to the defects

$$U_n = - \sum_{i,j} N_i \omega_{ij} \nu_{ij}, \quad (39)$$

$$U_p = - \sum_{i,j} N_i \omega_{ij} \pi_{ij}. \quad (40)$$

Here summation is carried out over all the defect states i and j . The minus signs in Eqs. (39)-(42) are introduced only in order that the rate would be positive when the number of carriers decreases and negative otherwise. Also, U_n and U_p could be considered as the resulting rates of losing the number of free carriers in the appropriate bands. One can also rewrite the Eqs. (39) and (40) via the rates of transitions by separate channels:

$$U_n = - \sum_{i,j} \sum_{\alpha} N_i \omega_{ij}^{(\alpha)} \nu_{ij}^{(\alpha)}, \quad (41)$$

$$U_p = - \sum_{i,j} \sum_{\alpha} N_i \omega_{ij}^{(\alpha)} \pi_{ij}^{(\alpha)}. \quad (42)$$

Note that the sums in Eqs.(39)-(42) include also diagonal terms, for which $j=i$, for example, the terms $-N_i \omega_{ii} \nu_{ii}$ in Eqs. (39) and (40). Each such addend gives the rate of carrier removal from a relevant band due to the static effect of

defects. In particular, if the static effects consist of the simultaneous capture of an electron and a hole by a defect (say in the i -th state) into one and the same electronic orbital, or of the change of band-to-band recombination rate because of the lattice distortion around the defects, then the recombination probability by such channels and the change of number of carriers in the bands will be: $\omega_{ii}^{(\alpha)} = T_{np}^{ii} np$, $\nu_{ii}^{(\alpha)} = \pi_{ii}^{(\alpha)} = 1$. Note that if $T_{np}^{ii} = (\tilde{\gamma}_i - \gamma) \cdot V_i$, where γ and $\tilde{\gamma}_i$ [$L^3 T^{-1}$] are the coefficients of the band-to-band recombination in the regular and distorted regions respectively, V_i is the volume of the region around the defect, then $\omega_{ii}^{(\alpha)}$ will give the additional probability of the band-to-band recombination to that in the absence of defects. In a stationary state both rates U_n and U_p are equal to each other, because predominance of one rate over the other would cause accumulation of one type of charge carriers, which is possible only at the non-stationary conditions. Proof of the assertion by Eqs. (37), (39), and (40) is discussed in Appendix B.

The quantity $U \equiv U_n = U_p$ is the rate of GR-transitions, which we are interested in. It is equal to the stationary rate of decreasing the number of the free carriers in either of the allowed bands due to the defects. Commonly, U is calculated in two steps: firstly, the system of kinetic equations is constructed and then solved. It gives the stationary distribution function of defects on states F_i , and then U is found by the one of the Eqs. (39)-(42). Further we shall describe how the equation for the rate of GR-transitions can be constructed using the digraph of states of defects G and other possibilities of the graph theory in investigation of the GR processes through point defects.

4.1.3. Construction of the Equation for the Rate of GR-transitions by Digraph of States

In order to find the rate U directly from a digraph of states G one should first build up all functional digraphs (to be

called hereafter as Φ -graphs) Φ_k covering G . Φ -graph is a cycle C (loop is also permitted) and, perhaps, some trees will grow into the vertices of the cycle [1], which form a forest. An important feature of a Φ -graph is that exactly one arc outgoes from each of its vertex. If one of the arcs will be removed from the cycle C of a Φ -graph, then the Φ -graph will turn into a tree growing into the vertex, which the removed arc is issued from. On the other hand, if the root vertex of a “growing into” tree will be connected by an arc with some other vertex of the tree, then the arc will close a cycle and a Φ -graph will appear. Any Φ -graph can be constructed by this way. If a Φ -graph includes all vertices and arcs of a digraph G , then one can say that such Φ -graph covers G . Fig. 8 shows an example of a digraph G with a Φ -graph covering G that contain multiple arcs corresponding to competing mechanisms. The Φ -graph consists of the cycle $C = 2 \rightarrow 5 \rightarrow 6 \rightarrow 2$ and of the forest, containing two trees: $T^{(2)} = 1 \rightarrow 2$ and $T^{(6)} = (7 \rightarrow 3) \& (4 \rightarrow 3 \rightarrow 6)$. Two Φ -graphs are considered as different, if their sets of arcs do not coincide. A digraph G may have several different Φ -graphs covering G . The subscript “ k ” at Φ_k is used to distinguish such Φ -graphs. For example, the digraph G in Fig. 9a may be covered by fourteen Φ -graphs Φ_k ($k = 1, \dots, 14$) shown in Fig. 9b. Not all digraphs have Φ -graphs covering them, but any strong digraph includes at least one covering Φ -graph. Further we shall deal with the strong digraphs only, because in steady state conditions all defects occupy the states belonging to the strong (sink) components of a digraph of states G . The defects populating any A -component can be studied independently from others. Weight[Φ_k] of a Φ -graph Φ_k is defined as the product of weights of all its arcs:

$$[\Phi_k] \equiv \prod_{i \rightarrow j \in \Phi_k} \omega_{ij}. \quad (43)$$

Let C_k be the cycle included into the Φ -graph Φ_k . Expected change of number of electrons in the conduction band and holes in the valence band occurring as a result of single passing of a defect along the cycle C_k we shall designate accordingly by ν_k and π_k :

$$\nu_k = \sum_{\substack{i \rightarrow j \in C_k \\ (C_k \in \Phi_k)}} \nu_{ij}, \quad (44)$$

$$\pi_k = \sum_{\substack{i \rightarrow j \in C_k \\ (C_k \in \Phi_k)}} \pi_{ij}. \quad (45)$$

In fact, magnitudes of ν_k and π_k coincide. One can believe it by summing up both sides of Eq.(38) along the cycle C_k and taking into account that at cyclic series of transitions the defect returns to the starting state, so that total change of number of electrons bound on it is equal to zero. Then one obtains the Eq. $\nu_k = \pi_k$.

Knowing the weights[Φ_k] of all Φ -graphs covering a digraph of states G , magnitudes of ν_k for the appropriate cycles C_k , and also the tree-weights[i] of all the M-vertices of the digraph G , one can find the rate of GR-transitions by

$$U = N_{\text{tot}} \cdot \frac{-\sum_k \nu_k [\Phi_k]}{\sum_{i=1}^M [i]}. \quad (46)$$

Here N_{tot} is concentration of defects. Note that instead of ν_k one can, of course, use the quantity π_k , which is equal to ν_k or, say, their symmetrical combination $(\nu_k + \pi_k)/2$. Proof of the Eq.(46), establishing the relationship between the digraph of states G and the rate of GR-transitions U , is in Appendix C. It follows from this equation, that contribution to U is coming only from those Φ -graphs Φ_k , for which the quantity ν_k is not equal to zero. For the Φ -graphs the cycle C_k assigns to the defect such a closed path, along which the number of free carriers averaged over the great number of passages varies. Sign of the contribution depends on whether the free carriers will be generated ($\nu_k > 0$) or removed ($\nu_k < 0$) when the defect passes along the cycle C_k . For $\nu_k > 0$ ($\nu_k < 0$), the contribution is negative (positive) in accordance with the above-mentioned convention on the sign of electronic transitions rate. The Φ -graphs with a cyclic path C_k , along which number of the free carriers does not vary (i.e. $\nu_k = \pi_k = 0$), do not make the contribution to the rate U .

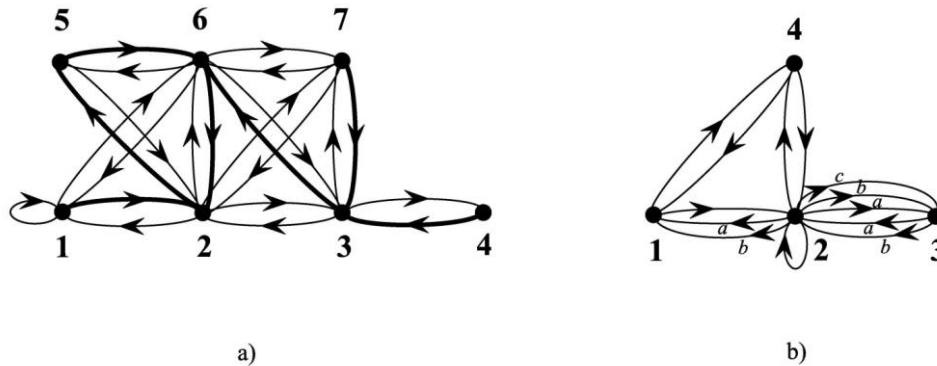


Figure 8. (a) Digraph G with one of its Φ -graphs. The arcs not included into this Φ -graph are plotted by dots. (b) An example of a digraph of states G with multiple arcs corresponding to the different mechanisms of the defect transitions

Eq. (46) is written through the quantities describing each transition, i.e. through the net probabilities of the transitions ω_{ij} and averaged over different mechanisms of transition quantities ν_k . It can also be written via the characteristics of separate mechanisms of transitions. Let a digraph $\mathbf{G}$ include an appropriate arc for each particular mechanism of transitions. Such a digraph will contain multiple arcs corresponding to competing mechanisms, as it is shown in Fig. 8b. Then any Φ -graph covering $\mathbf{G}$, will consist of the arcs corresponding to particular mechanisms. To underline this fact, we shall use a tag "tilde". For example, $\tilde{\Phi}_k$ and $\tilde{C}_k$ denote a Φ -graph and its cycle. Arcs of the cycle correspond to separate channels of transitions and according to the above definition, weight of the Φ -graph $[\tilde{\Phi}_k]$ will be equal to product of weights of all its arcs. Furthermore, it will be convenient to combine addends in the numerator in

$$[\tilde{\Phi}_k] \equiv \prod_{\substack{(\alpha) \\ i \rightarrow j \in \tilde{\Phi}_k}} \omega_{ij}^{(\alpha)}, \quad (47)$$

$$\tilde{\nu}_k \equiv \sum_{\substack{(\alpha) \\ i \rightarrow j \in \tilde{C}_k \\ (\tilde{C}_k \in \tilde{\Phi}_k)}} \nu_{ij}^{(\alpha)}. \quad (48)$$

Here $\tilde{\nu}_k$ is total change of number of conduction band electrons due to transitions of the defect along the cycle $\tilde{C}_k$ by the mechanisms, appropriate to this cycle. So, using the above definitions one can rewrite the Eq.(46) as:

$$U = N_{\text{tot}} \cdot \frac{-\sum_k \tilde{\nu}_k [\tilde{\Phi}_k]}{\sum_{i=1}^M [i]}. \quad (49)$$

Eq.(49). Let us first of all to note that all Φ -graphs $\tilde{\Phi}_k$ covering $\mathbf{G}$ can be divided into a few groups. In each of the groups all the Φ -graphs have the cycles $\tilde{C}_k$ passing the same vertices in the same direction, but only via different multiple arcs. It is convenient to use the notation $\tilde{C}_k^\mu$. Here the subscript k points to the group, and the superscript μ shows the numbers the cycles within the k -th group. It is evident that the same set of different forests will grow into any μ -th cycle of the same group k , and we shall designate this set of forests by Ψ_k . The forests are considered to be different, if composition of trees is different each from other. We shall define the total weight $[\Psi_k]$ of all set of forests as sum of weights of each concrete forest, and that of a single forest as a product of weights of all its trees, i.e. in fact as a product of weights of all arcs comprising this forest.

Then it is possible to present U as

$$U = N_{\text{tot}} \cdot \frac{-\sum_k \left\{ \sum_\mu \tilde{\nu}_k^\mu [\tilde{C}_k^\mu] \right\} \times [\Psi_k]}{\sum_{i=1}^M [i]}. \quad (50)$$

Here $\tilde{\nu}_k^\mu$ is the total (integer) change of number of free electrons caused by transitions of defects along the cycle $\tilde{C}_k^\mu$. Weight $[\tilde{C}_k^\mu]$ of the cycle is equal to product of weights of its arcs. Let us also note that if there are no trees grown into the cycles $\tilde{C}_k^\mu$ of the k -th group, then the weight $[\Psi_k]$ should be formally put equal to unity.

To clarify the above definitions let us consider the digraph $\mathbf{G}$ in Fig. 8b, which contains 14 cycles bunched in seven groups:

first group includes two cycles $\tilde{C}_1^l = 1 \rightarrow 4 \rightarrow 2 \rightarrow 1$ and $\tilde{C}_1^2 = 1 \rightarrow 4 \rightarrow 2 \rightarrow 1$, passing the vertices 1,4,2, and 1 in this order and is distinguished by the multiple arcs $2 \rightarrow 1$ and $2 \rightarrow 1$. Second group consists of one cycle $\tilde{C}_2^l = 1 \rightarrow 2 \rightarrow 4 \rightarrow 1$. Third group includes two cycles $\tilde{C}_3^l = 1 \rightarrow 2 \rightarrow 1$ and $\tilde{C}_3^2 = 1 \rightarrow 2 \rightarrow 1$. Fourth and fifth ones contain by one cycle $\tilde{C}_4^l = 1 \rightarrow 4 \rightarrow 1$ and $\tilde{C}_5^l = 2 \rightarrow 4 \rightarrow 2$, respectively. 6th group includes six cycles $\tilde{C}_6^l = 2 \rightarrow 3 \rightarrow 2$, $\tilde{C}_6^2 = 2 \rightarrow 3 \rightarrow 2$, $\tilde{C}_6^3 = 2 \rightarrow 3 \rightarrow 2$, $\tilde{C}_6^4 = 2 \rightarrow 3 \rightarrow 2$, $\tilde{C}_6^5 = 2 \rightarrow 3 \rightarrow 2$, $\tilde{C}_6^6 = 2 \rightarrow 3 \rightarrow 2$, and, finally, seventh group is the loop $\tilde{C}_7^l = 2 \rightarrow 2$. Two variants of forests grow into each of the two cycles of the first group: one forest consists of the tree $(3 \rightarrow 2)$ and another one consists of the tree $(3 \rightarrow 2)$. The same concerns to the cycle of the second group, so we can write $\Psi_1 = \Psi_2 = \left\{ \left(3 \xrightarrow{(a)} 2 \right), \left(3 \xrightarrow{(b)} 2 \right) \right\}$. Four types of forests grow into the cycles of the third group: $\Psi_3 = \left\{ (4 \rightarrow 1) \& \left(3 \xrightarrow{(a)} 2 \right), (4 \rightarrow 1) \& \left(3 \xrightarrow{(b)} 2 \right), (4 \rightarrow 2) \& \left(3 \xrightarrow{(a)} 2 \right), (4 \rightarrow 2) \& \left(3 \xrightarrow{(b)} 2 \right) \right\}$. Six variants of forests grow into the cycle $\tilde{C}_4^l$: $\Psi_4 = \left\{ \left(3 \xrightarrow{(a)} 2 \rightarrow 1 \right), \left(3 \xrightarrow{(a)} 2 \rightarrow 1 \right), \left(3 \xrightarrow{(b)} 2 \rightarrow 1 \right), \left(3 \xrightarrow{(b)} 2 \rightarrow 1 \right), \left(3 \xrightarrow{(a)} 2 \rightarrow 4 \right), \left(3 \xrightarrow{(b)} 2 \rightarrow 4 \right) \right\}$ and four forests grow into the cycle $\tilde{C}_5^l$: $\Psi_5 = \left\{ (3 \rightarrow 2) \& (1 \rightarrow 2), (3 \rightarrow 2) \& (1 \rightarrow 2), (3 \rightarrow 2) \& (1 \rightarrow 4), \right.$

^(b)
 $(3 \rightarrow 2) \& (1 \rightarrow 4)$. Three variants of forests grow into the cycles of the sixth group: $\Psi_6 = \{(1 \rightarrow 4 \rightarrow 2), (1 \rightarrow 2) \& (4 \rightarrow 2), (4 \rightarrow 1 \rightarrow 2)\}$ and, at last, six variants of forests grow into the sole vertex of the loop $\tilde{C}_7^I$. Each of them is a tree covering the digraph G : $\Psi_7 = \{(1 \rightarrow 4 \rightarrow 2) \& (3 \rightarrow 2), (1 \rightarrow 4 \rightarrow 2) \& (3 \rightarrow 2), (1 \rightarrow 2) \& (4 \rightarrow 2) \& (3 \rightarrow 2), (1 \rightarrow 2) \& (4 \rightarrow 2) \& (3 \rightarrow 2), (4 \rightarrow 1 \rightarrow 2) \& (3 \rightarrow 2), (4 \rightarrow 1 \rightarrow 2) \& (3 \rightarrow 2)\}$. Any of the forty eight Φ -graphs $\tilde{\Phi}_k$ ($k = 1, \dots, 48$) covering G is constructed by conjunction of one of these cycles with one of these forests growing into the chosen cycle. Hence, the numerator of Eq. (50) will contain 48 addends. Among them there will, for instance, be such ones: $\{\tilde{V}_I^I [\tilde{C}_I^I] + \tilde{V}_I^2 [\tilde{C}_I^2]\} \times [\Psi_I] = \{(V_{14} + V_{42} + V_{21}^{(a)}) \times \omega_{14} \omega_{42} \omega_{21}^{(a)} + (V_{14} + V_{42} + V_{21}^{(b)}) \times \omega_{14} \omega_{42} \omega_{21}^{(b)}\} \times (\omega_{32}^{(a)} + \omega_{32}^{(b)})$ and $\tilde{V}_7^I [\tilde{C}_7^I] [\Psi_7] = V_{22} \omega_{22} \times (\omega_{14} \omega_{42} \omega_{32}^{(a)} + \omega_{14} \omega_{42} \omega_{32}^{(b)} + \omega_{12} \omega_{42} \omega_{32}^{(a)} + \omega_{12} \omega_{42} \omega_{32}^{(b)} + \omega_{41} \omega_{12} \omega_{32}^{(a)} + \omega_{41} \omega_{12} \omega_{32}^{(b)})$. Note that the weight $[\Psi_7]$ coincides with the tree-weight of the 2nd vertex [2], and this is a general rule that if Ψ_k is a set of forests growing into the vertex i of a loop $i \rightarrow i$, then the weight $[\Psi_k]$ will give the tree-weight $[i]$ of this vertex.

In a non-degenerate case it is possible to make further progress, if in a model reverse transition is also taken into account together with each allowed transition. As shown in Appendix D, in this case the equation (50) becomes

$$U = N_{\text{tot}} \cdot \left(\frac{np}{n_i^2} - 1 \right) \cdot \frac{\sum_k \{ \sum_{\mu} \tilde{\rho}_k^{\mu} \tilde{V}_k^{\mu} [\tilde{C}_k^{\mu}] \} \times [\Psi_k]}{\sum_{i=1}^M [i]}. \quad (51)$$

In the summing on μ only those cycles $\tilde{C}_k^{\mu}$ are taken into

account which $\tilde{V}_k^{\mu} > 0$, and the following notation is used:

$$\tilde{\rho}_k^{\mu} \equiv \sum_{m=0}^{\tilde{V}_k^{\mu}-1} (np / n_i^2)^m. \quad (52)$$

Here n_i is the intrinsic concentration of carriers. The Eq. (51) demonstrates that for any model of defects which takes into account reverse transition for each of the transitions, in absence of degeneration, a characteristic factor $(np / n_i^2) - 1$ is present in the equation for the rate U . Since the rest fraction is positive, one can conclude that at high injection levels ($np > n_i^2$), $U > 0$, i.e. the rate of recombination will exceed the rate of generative transitions. Upon exclusion of the charge carriers ($np < n_i^2$), $U < 0$. Then the defects will play a role of centers for free carrier generation. At equilibrium state product of the free carrier densities $(np)_{eq}$ is equal to n_i^2 and the rate of GR-transitions U_{eq} equals to zero in complete agreement with the principle of detailed balance. Note that the equality $U_{eq} = 0$ can also be derived from the general Eq. (46) or from its variants Eqs. (49) and (50) which, distinct from the Eq. (51), holds true in the degenerated case (Appendix E).

It should be noted that the Eq. (51) is universal for all models of recombination through point defects. As we have tested, the equations for the rate of GR processes derived so far for particular models developed, e.g., by Shockley and Read³⁰, Hall³¹ for single level stable defects, by Evstropov³⁴ for recombination through excitons, by Karageorgy-Alkalaev, et. al. for donor-acceptor pairs³⁹ and hypothetic model of metastable defects⁴², by Kanaki et. al. for bistable defects²⁶ etc., are particular cases of the Eq. (51). Also, we note that the Eq. (51) has been derived without designing the system of kinetic equations. Preliminary knowledge on distribution of defects on states or derivation of it through mathematical manipulations was not needed. Analysis of Eq. (51) shows that the rate U contains the terms N_{tot} and $(np - n_i^2)$. Consequently, dependence of charge carrier lifetime on concentration of recombination centre $\tau \sim N_{tot}^{-1}$ as well as the approximation $U = \frac{\Delta n (\Delta p)}{\tau_{n,p}}$ are universal for all types of the centers from point defects.

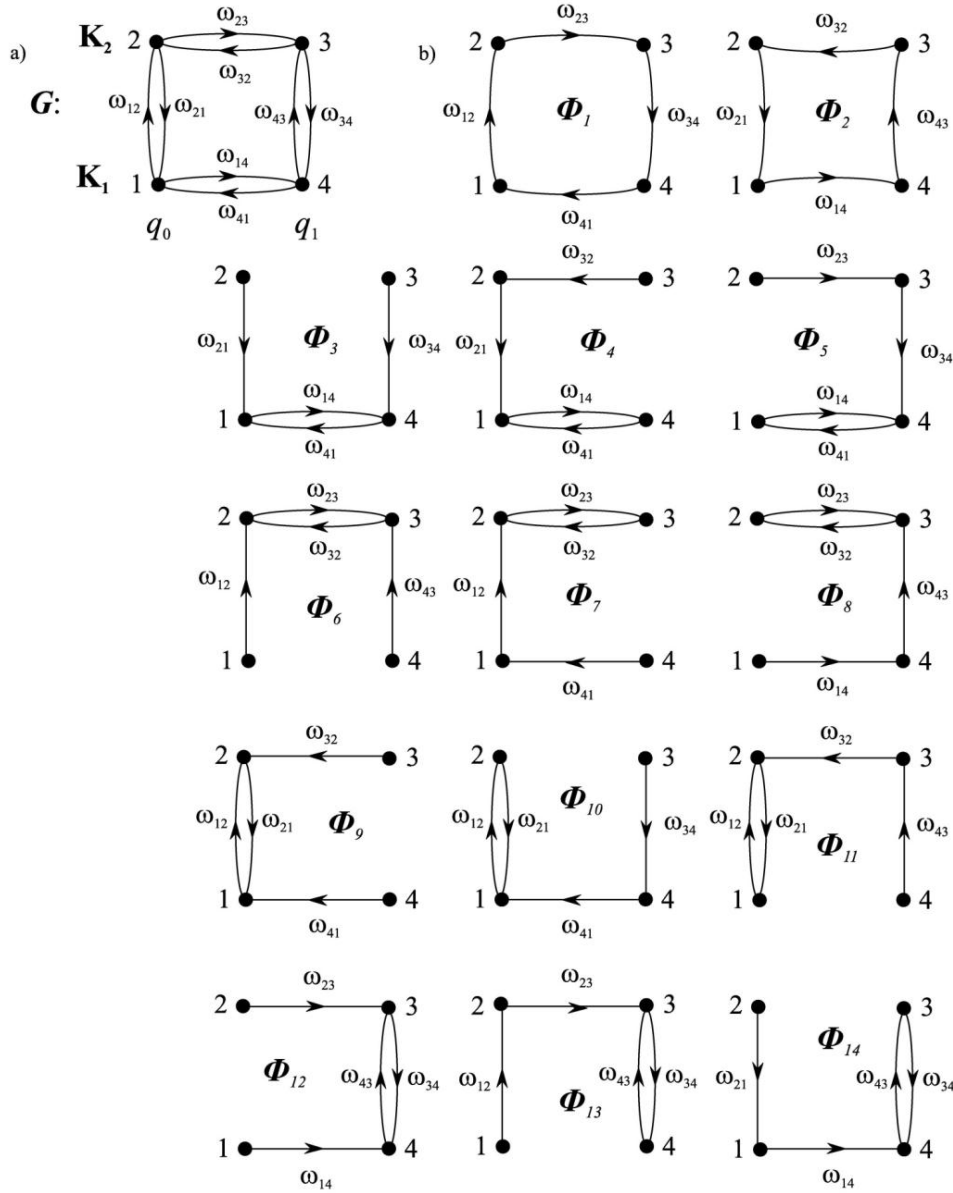


Figure 9. (a) Digraph of states G corresponding to a bistable defect, which can be either of its two-charge states with two ground states 1 and 4 and two excited states 2 and 3. Space configurations Q_1 and Q_2 correspond to the ground and excited states, respectively. In the states 1 and 2 the defect is ‘empty’ and is in the charge state q_0 . In the states 3 and 4 the defect has one captured electron and its charge is $q_1 = q_0 - 1$. (b) all Φ -graphs Φ_k ($k = 1, \dots, 14$) covering G . Weights of the Φ -graphs determine the rate of GR-transitions U

4.2. Application of the Results to Particular Models of Generation-recombination Processes

4.2.1. Astatic and Static Involvement of Defects in Generation-recombination Processes

By analysis of charge carrier GR we came to conclusion that participation of defects in these processes can be characterized as “astatic” and “static”. It can be said as static if as a result of recombination there is no change of charge state of the defect. Otherwise it can be considered as astatic. Fig. 7 (a)-(f) shows some examples of astatic and static involvements of a defect in charge carrier recombination. In Fig. 7(a)-(d) we display the examples of astatic involvement, which include: capture of a conduction band electron by a defect [Fig. 7a], recombination of the trapped electron with a

hole accompanied by transferring the energy to a free electron [Fig. 7b], band-band recombination of an electron-hole pair with some part of energy spent for excitation of an electron from the defect to the conduction band [Fig. 7c], simultaneous capture of one electron from the conduction band and another electron from the valence band [Fig. 7d]. These transitions are accompanied by recharging the defect by losing one electron [Fig. 7 (b), (c)], gaining one electron [Fig. 7 (a)] and [Fig. 7 (d)] two electrons. So, they can be called as astatic participation of the defect in the processes of generation and recombination. The processes can be accompanied by intra-center Auger transitions²² (not shown in the figures).

The examples of static involvement of defects in charge carrier recombination are shown in Figs. 7 (e) and (f). The

transition in Fig. 7(e) consists of capture of an electron from the conduction band and a hole from the valence band by the defect at the same time and this process does not change number of electrons at the defect and its charge state. However, the defect can nevertheless be passed into some other quantum state, if, e.g., an electron and a hole will be trapped into different electronic orbitals. In the latter case the defect “invisibly”, i.e. without any apparent consequences for itself, participates in the transition, providing an extra channel of recombination for electrons and holes. It should be emphasized that nature of this process is completely different from the one-electron mechanism of recombination when a defect captures a carrier of one type and only after that it captures another type of charge carrier. In our case we deal with capture of both types of charge carriers simultaneously. Note that the mechanism can result in discrepancy between the experimental data and the recombination rate calculated within the band-to-band recombination without including the defects into account. However, involvement of defects could be testified, for example, by radiation, which may accompany the transition, because it will differ from a mere band-to-band radiation, and also presence of dependence of band-to-band recombination rate on the density of defects. Also, it can be testified by difference of calculated and experimentally determined carrier lifetimes.

Similar to processes in Fig. 7(e), those in Fig. 7(f) do not cause recharging the defect. Distinct from the band-to-band recombination in the regular lattice, it is subjected to influence of the nearby defect [Fig. 7 (f), dotted line]. This influence can be, e.g., the result of transmission to the defect part of the energy liberated during carrier capture and of the momentum, initiating thus the intra-center transformation (not shown in the Fig. 7). The intra-center transformation can be the transition between different states of atomic multiplets or different space configurations of atoms. Also, the defects can influence a course of the band-band recombination indirectly without making any transitions at all. Indeed, any defect always distorts more or less vast region of the lattice, whereas the probability of the band-to-band recombination depends on the lattice. In regular lattice it can differ significantly from that in distorted one. If the volume of the distorted region around each defect is V_0 , then in the unit volume of the crystal the distorted volume should be $N_D V_0$, where N_D is a density of defects. So, if γ and $\tilde{\gamma}$ [$L^3 T^{-1}$] are the probabilities of the band-band recombination rates γ_{np} and $\tilde{\gamma}_{np}$ in undistorted and distorted lattice regions, respectively, then the average recombination rate per unit volume will be characterized by the effective constant $\gamma_{eff} = \gamma \times [1 - N_D V_0] + \tilde{\gamma} \times N_D V_0$, which exceeds γ by $\sim 10\%$ at $N_D = 10^{18} \text{ cm}^{-3}$, $V_0 \sim 10^{-20} \text{ cm}^3$ and $\tilde{\gamma}/\gamma = 10$. Both examples in Figs. 7 (e) and (f) display that influence of defects on a course of GR-transitions cannot, necessarily be accompanied by transitions of defects between their states, but also be (e) latent and (f) passive, be involved in the GR processes without changing their charge state. That is why involvement

of defects in such processes could naturally be termed as “static” in contrast to those (a-d) termed as “astatic”.

4.2.2. Rate of Static Mechanism of Recombination

Note that the defect in the i -th state can influence on the rate of electronic transitions in the system, without changing its charge state. On digraph of states $\mathbf{G}$ it is pointed out with a loop incident to the i -th vertex. This is quite natural: a loop, as well as any arc on a digraph of states, indicates some transition in the system with involvement of the defect, but such transition does not take the defect out of its state. Then the above equations for the rate of GR-transitions U may be split up into two terms U_{ast} and U_{st} :

$$U = U_{ast} + U_{st}. \quad (53)$$

Here U_{ast} is the rate of all GR-transitions accompanied with passage of the defects into the other charge state. By other words, U_{ast} is the rate of astatic transitions. This term includes all Φ -graphs. Cycles of the Φ -graphs contain two or more vertices. The other addend U_{st} is the rate of GR-transitions which occur with the static involvement of defects. U_{st} includes all Φ -graphs with loops. Separating the contribution from loops in the Eq. (50), one can get the equation for the rate of static GR-transitions:

$$U_{st} = N_{tot} \cdot \frac{- \sum_{i=1}^M \left\{ \sum_{\alpha} \nu_{ii}^{(\alpha)} \omega_{ii}^{(\alpha)} \right\} \times [i]}{\sum_{i=1}^M [i]}. \quad (54)$$

Here it has been taken into account that the weight $[\tilde{\mathcal{C}}_i^\alpha]$ of a loop $\tilde{\mathcal{C}}_i^\alpha$ is the weight $\omega_{ii}^{(\alpha)}$ of its sole arc $i \rightarrow i$, and the total weight $[\Psi_i]$ of all forests growing into the sole vertex i , gives the tree-weight $[i]$ of this vertex.

Here we will discuss the following important question as to when the static mechanisms of influence of defects on GR processes should be taken into account along with the astatic ones. Suppose that the recombination theory for a defect without static effects has already been developed. It can be, e.g., the theory developed by Shockley and Read³⁰, and Hall³¹ describing the single ionized defects without excited states. Digraph of states $\mathbf{G}$, corresponding to such defects has no loops in it. To account for the static mechanisms, one should add loops into the digraph $\mathbf{G}$. As mentioned earlier, the static mechanism does not take the defects out of their charge states, but influences on distribution function of the defects on their states and the rate of GR-transitions indirectly through variations of free charge carrier concentration. One could also come to this conclusion from the diagram point of view. Indeed, presence or absence of loops in $\mathbf{G}$ has no effect on tree-weights $[i]$ of vertices of $\mathbf{G}$, since the loops are not the part of the trees covering $\mathbf{G}$. Hence, the distribution function F_i which equals to the ratio of the tree-weight $[i]$ to the total tree-weight $[\mathbf{G}]$ of the digraph $\mathbf{G}$ [Eqs.(39)-(40)] remains unaffected by the loops. Presence of loops influences only on the second addend in Eq.(53), i.e.

on the static GR-transitions rate U_{st} , without affecting U_{ast} .

Based on the above-discussions one can say that static effects may be taken into consideration at any stage of developing the statistical theory of GR processes, since they can be studied irrespective of the static ones. Therefore, the recombination theory which does not include the static effects is not useless, because it provides us with the term U_{ast} in Eq.(53). If a defect has a noticeable static influence, then it will be enough first to calculate the rate of the static GR-transitions U_{st} using, e.g., the usual function of distribution of such defects known from SRH theory [Eq. (54)]. Then one should add the result to the astatic GR rate U_{ast} obtained within the framework of the above theory.

4.2.3. Examples of Constructing the Equation for the Rate of GR-transitions by a Digraph of States

As the first example we shall consider a defect with M-charge [Fig. 10], but without excited states described by a digraph of states $\mathbf{G}$ [Fig. 10a]. i -th vertex ($i = 1, \dots, M$) of the digraph corresponds to the defect with $(i-1)$ captured electrons. So the 1st vertex corresponds to the “empty” defect with a charge q_0 , the 2nd vertex corresponds to the defect with one captured electron and with a charge $q_1 = q_0 - 1$, etc. There are $(M-1)$ Φ -graphs Φ_k ($k = 1, \dots, M-1$) covering $\mathbf{G}$. As it is seen from Fig. 10b, the Φ -graph Φ_k consists of a cycle $C_k = k \rightarrow (k+1) \rightarrow k$ given by a couple of counter arcs linking the adjacent vertices k and $(k+1)$, and also of the trees $1 \rightarrow 2 \rightarrow \dots \rightarrow (k-1) \rightarrow k$ and $M \rightarrow (M-1) \rightarrow \dots \rightarrow (k+2) \rightarrow (k+1)$ growing into the vertex k and $(k+1)$ respectively. The terminal vertices 1 and M may be formally considered as roots of the trivial trees made up of only one vertex and have no arcs. Weight of such trees is assumed to be equal to unity. According to the Eq. (43), to find the weight of the Φ -graph one should multiply the weights of all of its arcs:

$$[\Phi_k] = \prod_{i=1}^k \omega_{i,i+1} \times \prod_{i=k}^{M-1} \omega_{i+1,i}. \quad (55)$$

Expected change of number of conduction band electrons due to the transitions of a defect along the arcs comprising the cycle C_k will be calculated by the Eq.(53):

$$v_{k,k+1} = \sum_{\alpha} v_{k,k+1}^{(\alpha)} \cdot \omega_{k,k+1}^{(\alpha)} / \omega_{k,k+1} \quad (56)$$

$$v_{k+1,k} = \sum_{\beta} v_{k+1,k}^{(\beta)} \cdot \omega_{k+1,k}^{(\beta)} / \omega_{k+1,k}. \quad (57)$$

The average change of the number of free electrons along this cycle will be equal to

$$v_k = v_{k,k+1} + v_{k+1,k}. \quad (58)$$

The sole tree $T^{(i)} = 1 \rightarrow 2 \rightarrow \dots \rightarrow (i-1) \rightarrow i \leftarrow (i+1) \leftarrow \dots \leftarrow (M-1) \leftarrow M$ grows into the i -th vertex of the digraph $\mathbf{G}$. It determines the tree-weight:

$$[i] = [T^{(i)}] = \prod_{j=1}^{i-1} \omega_{j,j+1} \times \prod_{j=i+1}^M \omega_{j,j-1}. \quad (59)$$

Let us now apply these results to Eq.(46):

$$U = N_{\text{tot}} \cdot \frac{- \sum_{k=1}^{M-1} (v_{k,k+1} + v_{k+1,k}) \times \prod_{i=1}^k \omega_{i,i+1} \times \prod_{i=k}^{M-1} \omega_{i+1,i}}{\sum_{i=1}^M \prod_{j=1}^{i-1} \omega_{j,j+1} \times \prod_{j=i+1}^M \omega_{j,j-1}} \quad (60)$$

By dividing numerator and denominator of the Eq. by the product of the probabilities of all consequent transitions from the state M into the state 1 $\omega_{M,M-1} \times \omega_{M-1,M-2} \times \dots \times \omega_{32} \times \omega_{21}$, use the notations:

$$R_1 \equiv 1 \quad (61)$$

$$R_i \equiv \prod_{j=1}^{i-1} (\omega_{j,j+1} / \omega_{j+1,j}) \text{ at } i = 2, \dots, M, \quad (62)$$

$$A_i \equiv - (v_{i,i+1} + v_{i+1,i}) \times \omega_{i,i+1}$$

$$= - \sum_{\alpha} v_{i,i+1}^{(\alpha)} \cdot \omega_{i,i+1}^{(\alpha)} - \frac{\omega_{i,i+1}}{\omega_{i+1,i}} \times \sum_{\beta} v_{i+1,i}^{(\beta)} \cdot \omega_{i+1,i}^{(\beta)} \quad (i = 1, \dots, M-1), \quad (63)$$

then

$$U = N_{\text{tot}} \cdot \frac{\sum_{i=1}^{M-1} A_i \times R_i}{\sum_{i=1}^M R_i}. \quad (64)$$

It should be noted that the Eq. (64) does not take into account the possible static influence of defects on GR-transitions. It only gives the contribution U_{ast} from transitions related to recharging the defects. When static mechanisms of recombination is present the digraph of states $\mathbf{G}$ should be supplemented with corresponding loops (Fig. 10c), which aside from the Φ -graphs [Fig. 10b] with cycles of length 2, provides the digraph $\mathbf{G}$ with the loopy Φ -graphs (Fig. 10d). The rate U_{st} of GR-transitions with static involvement of defects is given by Eq.(54), which can be rewritten in the following form:

$$U_{st} = N_{\text{tot}} \cdot \frac{\sum_{i=1}^M S_i \times R_i}{\sum_{i=1}^M R_i}, \quad (65)$$

where

$$S_i \equiv - \sum_{\alpha} v_{ii}^{(\alpha)} \omega_{ii}^{(\alpha)} \quad (i = 1, \dots, M). \quad (66)$$

Net rate of GR-transitions U is the sum of Eqs.(64) and (65). The non-degenerate case can be taken into account explicitly, by taking advantage of Eq.(51). In the same way one can obtain the following equation for U :

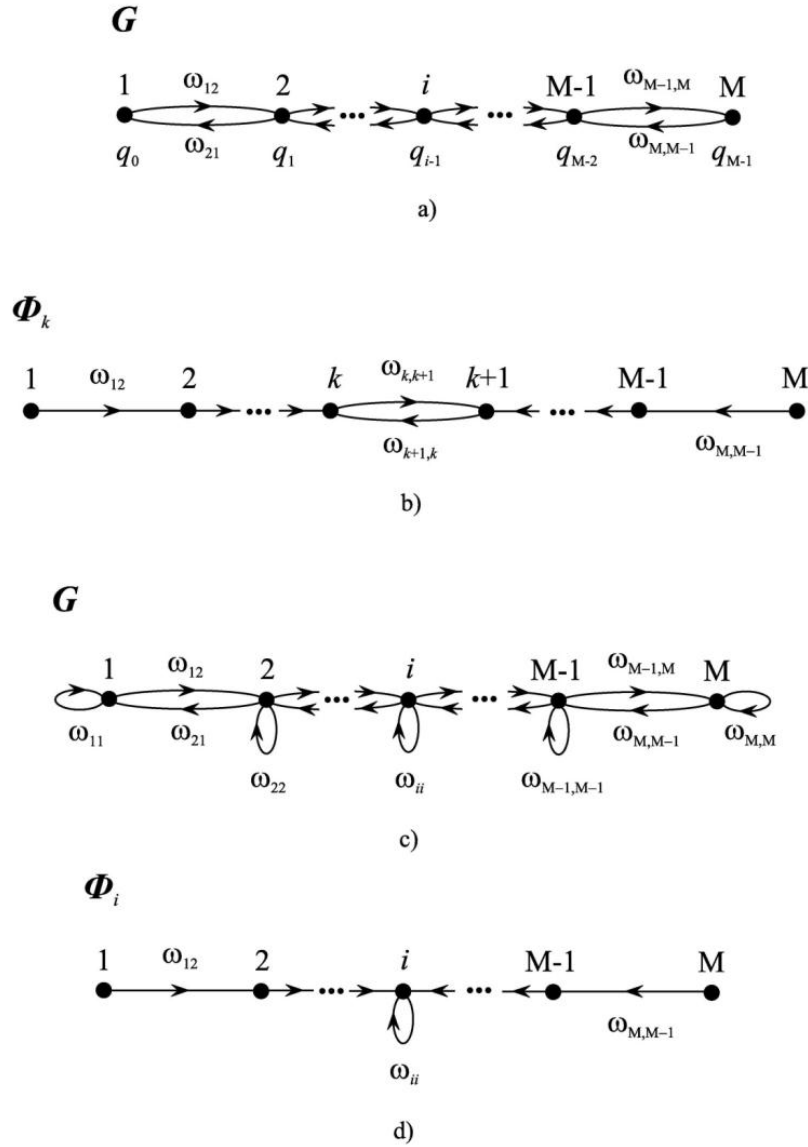


Figure 10. (a) M-vertex digraph of states G for M-charge defect without excited states. Absence of loops indicates that the static effects are neglected. (b) One of the $(M-1)$ Φ -graphs Φ_k ($k = 1, \dots, M-1$) covering the digraph G . (c) Digraph of states G of a defect of the above type, which accounts for both types of transitions with astatic and static influence. (d) Digraph G containing Φ -graphs Φ_i with the loops along with the Φ -graphs Φ_k .

$$U = N_{\text{tot}} \cdot \left(\frac{np}{n_i^2} - 1 \right) \cdot \frac{\sum_{k=1}^{M-1} a_k \times R_k}{\sum_{k=1}^M R_k}, \quad (67)$$

where R_k ($k = 1, \dots, M$) are defined in Eqs.(61) and (62), and the coefficients a_k are

$$a_k \equiv \frac{1}{\omega_{k+1,k}} \times \sum_{(\tilde{v}_k^\mu > 0)} \tilde{\rho}_k^\mu \tilde{v}_k^\mu [\tilde{C}_k^\mu] \quad (k = 1, \dots, M-1). \quad (68)$$

If it is possible to neglect the Auger processes, then the probability of capturing a conduction and a valence band electrons will be

$$\omega_{k,k+1}^{(C.B.)} = C_n^{k,k+1} n \quad (v_{k,k+1}^{(C.B.)} = -1) \quad (69)$$

and

$$\omega_{k,k+1}^{(V.B.)} = E_p^{k,k+1} \quad (v_{k,k+1}^{(V.B.)} = 0), \quad (70)$$

respectively. Probability of excitation of an electron from defect level to the conduction band will be

$$\omega_{k+1,k}^{(C.B.)} = E_n^{k+1,k} \quad (v_{k+1,k}^{(C.B.)} = +1), \quad (71)$$

and that to capture a hole from the valence band by a defect is

$$\omega_{k+1,k}^{(V.B.)} = C_p^{k+1,k} p \quad (v_{k+1,k}^{(V.B.)} = 0). \quad (72)$$

Thus, the defect has four ways of passing along the cycle

$C_k = k \rightarrow (k+1) \rightarrow k$: $\tilde{C}_k^1 = k \xrightarrow{(C.B.)} (k+1) \xrightarrow{(C.B.)} k$, $\tilde{C}_k^2 = k \xrightarrow{(V.B.)} (k+1) \xrightarrow{(V.B.)} k$, $\tilde{C}_k^3 = k \xrightarrow{(V.B.)} (k+1) \xrightarrow{(C.B.)} k$ and $\tilde{C}_k^4 = k \xrightarrow{(C.B.)} (k+1) \xrightarrow{(V.B.)} k$. Here $C.B.$ and $V.B.$ on the arrows indicate the band, which interchanges by carriers with the defect level.

Let us now calculate total change of the number of conduction band electrons along each of the cycles:

$$\begin{aligned}\tilde{V}_k^1 &= \nu_{k,k+1}^{(C.B.)} + \nu_{k+1,k}^{(C.B.)} = 0, \quad \tilde{V}_k^2 = \nu_{k,k+1}^{(C.B.)} + \nu_{k+1,k}^{(V.B.)} = -1, \quad \tilde{V}_k^3 \\ &= \nu_{k,k+1}^{(V.B.)} + \nu_{k+1,k}^{(C.B.)} = +1, \quad \tilde{V}_k^4 = \nu_{k,k+1}^{(V.B.)} + \nu_{k+1,k}^{(V.B.)} = 0. \quad (73)\end{aligned}$$

As it is seen, the only cycle $\tilde{C}_k^3$ gives positive $\tilde{V}_k^\mu$ and, consequently, it is the only cycle that should be taken into account at calculation of the coefficients a_k in Eq.(68). Weight of the cycle is

$$[\tilde{C}_k^3] = \omega_{k,k+1}^{(V.B.)} \cdot \omega_{k+1,k}^{(C.B.)} = E_n^{k+1,k} \cdot E_p^{k,k+1}. \quad (74)$$

The factor $\tilde{\rho}_k^3$, calculated by Eq. (52), is equal to unity.

Thus, the coefficients a_k become

$$a_k = E_n^{k+1,k} \cdot E_p^{k,k+1} / (C_p^{k+1,k} p + E_n^{k+1,k}) \quad (k = 1, \dots, M-1). \quad (75)$$

$R_1 = 1$ and

$$R_k = \prod_{i=1}^{k-1} (C_n^{i,i+1} n + E_p^{i,i+1}) / (C_p^{i+1,i} p + E_n^{i+1,i}) \quad (76)$$

at $k = 2, \dots, M$. For defects with two charge states ($M = 2$) the Eq. (67) together with Eqs.(75) and (76) turn into the well-known equation in the Shockley-Read-Hall recombination theory^{30, 31}. For the M -charge defects the results of Refs.^{33, 35} can be obtained. As another example of constructing the equation for U we shall consider a four-vertex digraph of states G shown in Fig. 9a, describing, for example, bistable defects with two different charge states q_0 and q_1 . Two different configurations Q_1 and Q_2 correspond to each of the states. The transitions $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$ keep the charge of the defect constant and correspond to its transformation, whilst the transitions $1 \leftrightarrow 4$ and $2 \leftrightarrow 3$ are accompanied with recharging of the defect without changing its space configuration. The transitions $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$, corresponding to recharging of the defect simultaneously with configurational changes have not been included into the model. Theory of recombination through such defects was studied, in particular, in Ref.^{26, 41} within the kinetic approach⁴¹ and graph theory²⁶.

Furthermore, in previous chapter distribution function has been derived using the digraph of states G :

$$\begin{cases} F_1 = \frac{\omega_{43}\omega_{32}\omega_{21} + \omega_{23}\omega_{34}\omega_{41} + \omega_{32}\omega_{21}\omega_{41} + \omega_{34}\omega_{41}\omega_{21}}{D}, \\ F_2 = \frac{\omega_{12}\omega_{32}\omega_{43} + \omega_{14}\omega_{43}\omega_{32} + \omega_{41}\omega_{12}\omega_{32} + \omega_{34}\omega_{41}\omega_{12}}{D}, \\ F_3 = \frac{\omega_{12}\omega_{23}\omega_{43} + \omega_{14}\omega_{43}\omega_{23} + \omega_{41}\omega_{12}\omega_{23} + \omega_{21}\omega_{14}\omega_{43}}{D}, \\ F_4 = \frac{\omega_{12}\omega_{23}\omega_{34} + \omega_{14}\omega_{23}\omega_{34} + \omega_{32}\omega_{21}\omega_{14} + \omega_{21}\omega_{14}\omega_{34}}{D}. \end{cases} \quad (77)$$

Here the denominator D is the sum of the numerators of all of these fractions. Further we shall assume that the charge q_0 corresponds to the “empty” defect, and $q_1 = q_0 - 1$ to the defect with one trapped electron. Then in the non-degenerate case and upon neglecting the Auger effects, probabilities of transitions with recharging the defect will be: $\omega_4 = C_n^{14} n + E_p^{14}$, $\omega_{41} = C_p^{41} p + E_n^{41}$, $\omega_{23} = C_n^{23} n + E_p^{23}$, $\omega_{32} = C_p^{32} p + E_n^{32}$. Probabilities of configurational transitions ω_{12} , ω_{21} , ω_{34} and ω_{43} will be determined by the mechanisms of

passing of components of the defect between different positions in a crystal lattice. Also, we assume that free carriers do not participate in these transitions. In this case the latter probabilities will be independent on n and p .

The digraph under consideration has 14 Φ -graphs Φ_k ($k = 1, \dots, 14$) shown in Fig. 9b. The Φ -graph Φ_1 contains the cycle $C_1 = 1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$, Φ_2 includes the $C_2 = 1 \rightarrow 4 \rightarrow 3 \rightarrow 2 \rightarrow 1$, $\Phi_{3,4,5}$ contains of $C_3 = 1 \rightarrow 4 \rightarrow 1$, $\Phi_{6,7,8}$ contains $C_4 = 2 \rightarrow 3 \rightarrow 2$, $\Phi_{9,10,11}$ contains $C_5 = 1 \rightarrow 2 \rightarrow 1$ and $\Phi_{12,13,14}$ contains $C_6 = 3 \rightarrow 4 \rightarrow 3$. In a non-degenerate case, one can derive the equation for U from the Eq.(51). The cycle C_1 can be passed by four ways distinguished each from other by mechanisms of transitions

along the path $\tilde{C}_1^1 = 1 \xrightarrow{\omega_{12};0} 2 \xrightarrow{C_n^{23}n;-1} 3 \xrightarrow{\omega_{34};0} 4 \xrightarrow{C_p^{41}p;0} 1$, or $\tilde{C}_1^2 = 1 \xrightarrow{\omega_{12};0} 2 \xrightarrow{C_n^{23}n;-1} 3 \xrightarrow{\omega_{34};0} 4 \xrightarrow{E_n^{41};+1} 1$, or $\tilde{C}_1^3 = 1 \xrightarrow{\omega_{12};0} 2 \xrightarrow{E_p^{23};0} 3 \xrightarrow{\omega_{34};0} 4 \xrightarrow{C_p^{41}p;0} 1$, or, at last, $\tilde{C}_1^4 = 1 \xrightarrow{\omega_{12};0} 2 \xrightarrow{E_p^{23};0} 3 \xrightarrow{\omega_{34};0} 4 \xrightarrow{E_n^{41};+1} 1$.

The two parameters located above the arrows correspond to the probability $\omega_{ij}^{(\alpha)}$ of transition by the channel α and to the change of the number of conduction band electrons $\nu_{ij}^{(\alpha)}$.

Let us now count up the total changes of the number of free electrons for these cycles: $\tilde{V}_1^1 = 0 - 1 + 0 + 0 = -1$, $\tilde{V}_1^2 = 0 - 1 + 0 + 1 = 0$, $\tilde{V}_1^3 = 0 + 0 + 0 + 0 = 0$ and $\tilde{V}_1^4 = 0 + 0 + 0 + 1 = 1$. Among all of these cycles the only cycle $\tilde{C}_1^4$ has the positive $\tilde{V}_k^\mu$, so we need the weight of only this cycle $[\tilde{C}_1^4] = \omega_{12} E_p^{23} \omega_{34} E_n^{41}$ and the sum in Eq.(52) equals $\tilde{\rho}_1^4 = 1$. We shall now consider the next cycle C_2 . It can also be passed by four ways:

$\tilde{C}_2^1 = 1 \xrightarrow{C_n^{14}n;-1} 4 \xrightarrow{\omega_{43};0} 3 \xrightarrow{C_p^{32}p;0} 2 \xrightarrow{\omega_{21};0} 1$ ($\tilde{V}_2^1 = -1$),
 $\tilde{C}_2^2 = 1 \xrightarrow{C_n^{14}n;-1} 4 \xrightarrow{\omega_{43};0} 3 \xrightarrow{E_n^{32};+1} 2 \xrightarrow{\omega_{21};0} 1$ ($\tilde{V}_2^2 = 0$),
 $\tilde{C}_2^3 = 1 \xrightarrow{E_p^{14};0} 4 \xrightarrow{\omega_{43};0} 3 \xrightarrow{C_p^{32}p;0} 2 \xrightarrow{\omega_{21};0} 1$ ($\tilde{V}_2^3 = 0$) and
 $\tilde{C}_2^4 = 1 \xrightarrow{E_p^{14};0} 4 \xrightarrow{\omega_{43};0} 3 \xrightarrow{E_n^{32};+1} 2 \xrightarrow{\omega_{21};0} 1$ ($\tilde{V}_2^4 = 1$). Among the ways only $\tilde{C}_2^4$ is of interest: $[\tilde{C}_2^4] = E_p^{14} \omega_{43} E_n^{32} \omega_{21}$ and $\tilde{\rho}_2^4 = 1$. One can see from Fig. 9b that there are no trees grown into the cycles C_1 and C_2 except the trivial ones. According to the remark to the Eq. (50), weights of the forests $[\Psi_1]$ and $[\Psi_2]$, included into the Eq.(51), are equal to unity. Further, there are the following ways to pass the cycles C_3 and C_4 : $\tilde{C}_3^1 = 1 \xrightarrow{C_n^{14}n;-1} 4 \xrightarrow{C_p^{41}p;0} 1$ ($\tilde{V}_3^1 = -1$), $\tilde{C}_3^2$

$$= 1 \xrightarrow{C_n^{14} n; -1} 4 \xrightarrow{E_n^{41}; +1} 1 \quad (\tilde{V}_3^2 = 0), \quad \tilde{C}_3^3 = 1 \xrightarrow{E_p^{14}; 0} 4 \xrightarrow{C_p^{41} p; 0} 1 \quad (\tilde{V}_3^3 = 0),$$

$$\tilde{C}_3^4 = 1 \xrightarrow{E_p^{14}; 0} 4 \xrightarrow{E_n^{41}; +1} 1 \quad (\tilde{V}_3^4 = 1), \quad \tilde{C}_4^2 = 2 \xrightarrow{C_n^{23} n; -1} 3 \xrightarrow{E_p^{32} p; 0} 2 \quad (\tilde{V}_4^1 = -1),$$

$$\tilde{C}_4^2 = 2 \xrightarrow{C_n^{23} n; -1} 3 \xrightarrow{E_n^{32}; +1} 2 \quad (\tilde{V}_4^2 = 0),$$

$$\tilde{C}_4^3 = 2 \xrightarrow{E_p^{23}; 0} 3 \xrightarrow{C_p^{32} p; 0} 2 \quad (\tilde{V}_4^3 = 0), \quad \tilde{C}_4^4 = 2 \xrightarrow{E_p^{23}; 0} 3 \xrightarrow{E_n^{32}; +1} 2 \quad (\tilde{V}_4^4 = 1).$$

Among them only two ways have positive increments of the number of free electrons with weights $[\tilde{C}_3^4]$ and $[\tilde{C}_4^4]$ are $E_p^{14} E_n^{41}$ and $E_p^{23} E_n^{32}$. Sums in Eq.(52) for the weights are equal to unity: $\tilde{\rho}_3^4 = \tilde{\rho}_4^4 = 1$. Three versions of forests grow into the cycle C_3 : one of them consists of two trees ($2 \rightarrow 1$) and ($3 \rightarrow 4$). The forest together with the cycle C_3 produce the Φ -graph Φ_3 . Second one is the sole tree ($3 \rightarrow 2 \rightarrow 1$), which is well seen from Φ_4 . Third one is the tree ($2 \rightarrow 3 \rightarrow 4$) (see Φ_5). Total weight of all these forests is $[\Psi_3] = \omega_{21}\omega_{34} + \omega_{32}\omega_{21} + \omega_{23}\omega_{34}$. Three different forests also grow into the cycle C_4 : one of them includes two trees ($1 \rightarrow 2$) and ($4 \rightarrow 3$). Another one includes the tree ($4 \rightarrow 1 \rightarrow 2$) and the last one is the tree ($1 \rightarrow 4 \rightarrow 3$), so that $[\Psi_4] = \omega_{12}\omega_{43} + \omega_{41}\omega_{12} + \omega_{14}\omega_{43}$. Finally, both cycles C_5 and C_6 consist of the intra-center transitions $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$, which do not change numbers of free electrons ($v_{12} = v_{21} = 0$ and $v_{34} = v_{43} = 0$). Hence, the Φ -graphs $\Phi_{9...14}$ which contain these cycles do not make a contribution into the rate U . Now we should substitute these results into the Eq. (51), which yields the equation for the rate of astatic GR-transitions via the given defects:

$$U = N_{\text{tot}} \cdot \left(\frac{np}{n_i^2} - 1 \right) \cdot \frac{[\tilde{C}_1^4] + [\tilde{C}_2^4] + [\tilde{C}_3^4] \times [\Psi_3] + [\tilde{C}_4^4] \times [\Psi_4]}{D} = N_{\text{tot}} \cdot \left(\frac{np}{n_i^2} - 1 \right) \cdot \frac{Z}{D}, \quad (78)$$

with the factor

$$Z = E_p^{23} E_n^{41} \omega_{12}\omega_{34} + E_p^{14} E_n^{32} \omega_{43}\omega_{21} + E_p^{14} E_n^{41} (\omega_{21}\omega_{34} + \omega_{32}\omega_{21} + \omega_{23}\omega_{34}) + E_p^{23} E_n^{32} (\omega_{12}\omega_{43} + \omega_{41}\omega_{12} + \omega_{14}\omega_{43}) \quad (79)$$

and the denominator D which has been defined earlier.

4.2.4. Inertial Properties of An Ensemble of Defects at High Injection Levels

In this section we shall consider the question related to influence of defects on the rate of GR-transitions at high levels of injection of charge carriers. This leads to the problem of finding asymptotical behaviour of U at large concentrations n and p , because lifetimes of the charge carriers and GR-currents in power devices depend on these

parameters. Some defects are capable of providing high GR-transition rate at high injection levels. Such defects can be referred to as “inertialess”, meaning their capability to capture carriers of both signs without any time delay. Even if there is some time-lag then it drops fast with increasing the injection level. Some defects might show resistance or disinclination to GR processes. As a result they can provide only limited recombination rate, which tends to some finite value (e.g., to zero) as the injection level increases. Such defects should be classified as “inertial”, since the defects will spend on more time in the recombination-passive state without capturing the injected carriers. It leads to lagging of recombination rate compared to increase of the number of injected carriers.

There is also third type of defects with the rate of GR-transitions equal to zero at any levels of injection. These are, for example, the so-called sticking centers, exchanging by charge carriers with only one of the allowed bands. On the one hand inertial properties of an ensemble of defects will depend on the pumping condition. The Shockley-Read-Hall type recombination centers, e.g., might become inertial at single carrier injection as well, since U reaches its maximal value determined by concentration of charge carriers. On the other hand, inertial properties depend on the scheme of allowed transitions of defects, i.e. on the properties of a digraph of states G . In this section we shall derive those features of G that make the ensemble of defects inertial or inertialess, considering non-degenerate case and excluding the Auger processes from consideration. Here we shall formulate the criterion of lack of inertness, which is common for any types of defects.

We shall ascertain the expected asymptotical behaviour of the GR-transition rate U in a non-degenerate system excluding the Auger processes from consideration. In these conditions probability of transitions of the defects by capturing the electrons from the allowed bands is $\omega_j = C_n^{ij} n + E_p^{ij}$. The rate of emission of an electron from the defects is $\omega_j = C_p^{ij} p + E_n^{ij}$. Probabilities of intra-center transitions are assumed to be independent of the free carrier concentrations. Concentrations of the injected carriers will further be termed as “the parameters of excitation” (abbreviated to “PE”). For pumping of only electrons (holes) PE is the concentration of only electrons n (holes p). For bipolar carrier injection the role of PE will play both n and p . Then it is seen that the probabilities of any transitions in the system at high levels of injection will be proportional to the 0th or 1st degree of PE: $\omega_j \propto \text{PE}^0$ or $\omega_j \propto \text{PE}^1$ (in another notation, $\deg \omega_j = 0$ and $\deg \omega_j = 1$). Under these circumstances for the inertialess defects the asymptotic dependence of U on the injection level cannot be other than linear, i.e. $U \propto \text{PE}^1$. Indeed concentrations of defects N_i ($i = 1, \dots, M$) should tend to their constant asymptotic values as the injection level increases, so that $\max_{i=1, \dots, M} \{\deg N_i\} = 0$ and, in virtue of Eq.(53),

$$\deg U = \max_{i,j=1, \dots, M} \{\deg N_i \omega_{i,j} v_{i,j}\} = \max_{i,j=1, \dots, M} \{\deg \omega_{i,j}\} = 1.$$

It should be noted here that this is the particular case of more general statement which says that if the maximal possible magnitude of the exponent (k) in the dependence of the transition probabilities ω_{ij} on PE is, say, $k_{\max}$, then the exponent k in the asymptotic dependence $U \propto PE^k$ may be varied up to $k_{\max}$ (it can be proven just as the above case). When $k_{\max} = 1$, one can deal with the above case. So, the ensemble of defects to be considered as inertialess there must be probabilities with positive sign of the exponents. However, this requirement, which is usually fulfilled, is only the necessary one, but not sufficient yet. For non-degenerate system without Auger effects included into consideration one more necessary requirement of lack of inertness is active: carrier injection must be bipolar, otherwise the ensemble of defects will be inertial. This is a merely consequence of a more general statement that U may reach its maximal possible value of exponent $k = k_{\max}$ only at bipolar carrier injection. About inertial defects one can say they can lead to power dependence of the recombination rate $U \propto PE^d$. Here d is integer, which can be varied in the range:

$$s - M + 1 \leq d \leq 0. \quad (80)$$

Here shows the way of pumping: $s = 2$ for bipolar and $s = 1$ for single-polar pumping (proof is given in Appendix G). Exact magnitude of d will depend on peculiarities of the scheme of allowed transitions. Therefore, before making some calculations one may conclude that the ensemble of defects with, say, four different quantum states can be inertialess and will lead to the asymptotic dependence $U \propto PE^1$ or it can be inertial and can manifest one of the following dependencies:

$$U \propto PE^0, U \propto 1/PE, U \propto 1/PE^2. \quad (81)$$

The last one is possible only for the single-polar injection. It might happen that the ensemble may turn out to make no contribution to the GR-transitions rate at any pumping conditions. Now we shall clarify the features of the scheme of transitions that would show whether the defect is inertialess or not. It follows from Eq. (54) that a defect can be inertialess, i.e. will provide the asymptotic rate $U \propto PE^1$, only if there is at least one such defect state i of concentration N_i , which will not tend to zero as the injection level increases (i.e. $N_i \propto PE^0$) and if there is at least one transition $i \rightarrow i_l$ with the probability $\omega_{ii_l}^{(\alpha)}$ proportional to PE^1 . Let us write down the equation for the defect density N_i through the tree-weights of vertices of the digraph of states G :

$$N_i = N_{\text{tot}} \times [i] / \sum_{j=1}^M [j]. \quad (82)$$

In an asymptotical limit weight of any state $[j]$ will be determined by only those trees $T^{(j)}$ covering G with weights increasing most fast with increasing the carrier concentration. If weights of these trees, growing into the j -th vertex, increase proportionally to PE^{t_j} , then the same proportionality $[j] \propto PE^{t_j}$ will take place for the tree-weight of an appropriate state. t_j coincides with number of arcs of the tree $T^{(j)}$ with weights proportional to PE^1 . Therefore,

population of the state i will not become vanishing only if the vertex i is a root of at least one tree $T_{\max}^{(i)}$ with maximal parameter $t_{\max} \equiv \max_{j=1, \dots, M} \{t_j\}$. Thus, for the ensemble of defects to be inertialess it is necessary and sufficient, that an arc $i \rightarrow i_l$ of weight $\omega_{ii_l}^{(\alpha)} \propto PE^1$ will be issued from the vertex i , which is a root of a tree of asymptotical weight $[T_{\max}^{(i)}] \propto PE^{t_{\max}}$. Then in the digraph G there will necessarily be such a tree, growing into the vertex i_l with weight proportional to $PE^{t_{\max}}$. An arc will exist issued from the vertex i_l with the weight proportional to PE^1 . If one removes an arc, e.g., $i_l \rightarrow i_2$ from the tree $T_{\max}^{(i)}$ and adds another one $i \rightarrow i_l$, then one can get a new tree $T^{(i_l)}$ growing into the vertex i_l with $\deg[T^{(i_l)}] = \deg[T_{\max}^{(i)}] + \deg \omega_{ii_l}^{(\alpha)} - \deg \omega_{i_l i_2}^{(\beta)} = t_{\max} + 1 - \deg \omega_{i_l i_2}^{(\beta)}$. Since the degree in the power t_{i_l} of the weight of the tree $T^{(i_l)}$ cannot exceed the maximum value $t_{\max}$ and that the probability of any transition, including $i_l \rightarrow i_2$ can be proportional to only PE^0 or PE^1 , one comes with necessity to equalities $\deg[T^{(i_l)}] = t_{\max}$ and $\deg \omega_{i_l i_2}^{(\beta)} = 1$. For the same reasons it will turn out that the vertex i_2 will be a root of at least one tree of maximal asymptotical weight proportional to $PE^{t_{\max}}$. Also, an arc issued from this vertex with weight proportional to PE^1 . Following this way we can pick up a set of vertices $i, i_l, i_2, \dots, i_N$ of the digraph G , which are mutually connected with the arcs with weights proportional to PE^1 . Each of the vertices is a root of the trees with weights proportional to $PE^{t_{\max}}$. Hence, one can conclude that the ensemble of defects can be said to be inertialess in the following cases:

- 1) The digraph of states G has such a subset of vertices, which are mutually reachable with the arcs with weights proportional to PE^1 . Such a subset of vertices will further be referred as "non-inertial recombination component" (NIRC);
- 2) The tree-weights of vertices in a NIRC must have the greatest possible growth rate, i.e. be proportional to $PE^{t_{\max}}$. It is sufficient for the weight of at least one vertices of NIRC to have such an asymptotic limit, because the weights in asymptotical limit are proportional to each other. This note comes out from the following statement of the graph theory: if a group of vertices of a digraph G are connected by the arcs of equal and maximal weight in such a manner that all of them are mutually reachable, then the heaviest trees covering G and growing into these vertices will be of equal weight and, therefore, will contribute equally to the tree-weights of the vertices.

Both signatures of lack of inertness of recombination properties can easily be tested for any complicated scheme of allowed transitions of defects. Before discussing the inertial properties of defects within the framework of the graph

theory, we would like to specify their physical meaning. As it is clear from definition, a NIRC is such a group of defect states, which by capturing a free electron(hole) can be immediately ready to capture a hole(electron). Depending on features of the scheme of allowed transitions and of injection conditions the digraph of the defect states $\mathbf{G}$ may have one or more NIRC's, or no NIRC at all. In case of single polar injection presence of NIRC becomes impossible. For a defect to be able to make a *cyclic* passage within a NIRC by capturing the injected carriers, it should capture the same number of electrons and holes, which implies bipolar injection. So, being in any non-inertial state a defect turns out to be able to capture any type of free carrier, and probability of such captures will increase with increasing PE.

A question arises as to what happens if a defect abandons the NIRC? There are two possibilities. One of them is the defect can immediately or during the time of order PE^{-1} passes into another NIRC, and will again be recombination-active. It can also pass into another state and be unable to capture the injected carriers. Such states are termed as "recombination-passive" (RP). The defect can quite the RP-state due to transition with probability proportional to PE^0 , intra-center transition, transition accompanied with generation of a free carrier, but not capture, or single polar injection. A defect being in a certain RP-state can be out of the recombination activity for some time at any level of injection. Such defects will hamper the rate of GR-processes. Therefore, for an ensemble of defects to be non-inertial the scheme of allowed transitions must have at least one NIRC, i.e. such groups of defect states, which have no impediments for carrier recombination. This is the first reprint related to lack of inertness of defects. The other possibility is that the average time to be spent by a defect in the NIRC's, i.e. the lifetimes of the NIRC-states, should not tend to zero with increasing the injection level. Otherwise number of the recombination active defect states will vanish with increasing the number of free carriers. It is in favour of population of RP-states resulting in inhibition of recombination. This is the second point of the above condition. Note that here we have used implicitly the ergodic properties of the steady state. The relative portion of time, which a defect spends in such a quantum state, coincides with that for all defects of the ensemble, which occupy the state at any time. As an example we shall construct asymptotic equation for the recombination rate through the donor-acceptor pairs (DA-pairs). In the simplest case the DA-pair can be in four different states: $[\mathbf{D}^+\mathbf{A}^0]$, $[\mathbf{D}^0\mathbf{A}^0]$, $[\mathbf{D}^+\mathbf{A}^-]$ and $[\mathbf{D}^0\mathbf{A}^-]$ [Fig.11], which are associated with the vertices 1, 2, 3, and 4 of the digraph $\mathbf{G}$ in Fig.11a. In an "empty" state $[\mathbf{D}^+\mathbf{A}^0]$ the donor level is ionized, and the acceptor is neutral, so a charge of the pair is $q_0 = +1$. In the states $[\mathbf{D}^0\mathbf{A}^0]$ and $[\mathbf{D}^+\mathbf{A}^-]$ one captured electron is located in the donor or in the acceptor level, respectively. Therefore in both of the states the pair is electrically neutral: $q_1 = 0$. In the state $[\mathbf{D}^0\mathbf{A}^-]$ the donor is neutral, and the acceptor is ionized. So the charge is $q_2 = -1$. The transition $1 \rightarrow 2$ is capture of an electron from an allowed band which will be localized on the donor. Probability of this process is $\omega_2 = C_n^{12}n + E_p^{12}$. One

can get $\omega_{21} = C_p^{21}p + E_n^{21}$ for the reverse transition, $\omega_{13} = C_n^{13}n + E_p^{13}$ for the electron-capture from an allowed band into the acceptor, and $\omega_{31} = C_p^{31}p + E_n^{31}$ for the reverse process. Probabilities of the remaining transitions are $\omega_{24} = C_n^{24}n + E_p^{24}$, $\omega_{42} = C_p^{42}p + E_n^{42}$, $\omega_{34} = C_n^{34}n + E_p^{34}$, $\omega_{43} = C_p^{43}p + E_n^{43}$. Probabilities of intra-center transitions ω_{23} and ω_{32} do not depend on free carrier concentrations. According to Eq.(54) the rate of GR-transitions through such defects is given by the equation

$$U = N_1 C_n^{12} n + N_1 C_n^{13} n + N_2 C_n^{24} n + N_3 C_n^{34} n - N_4 E_n^{42} - N_4 E_n^{43} - N_3 E_n^{31} - N_2 E_n^{21}. \quad (83)$$

For bipolar carrier injection both concentrations n and p play the role of the PE. For all vertices being mutually reachable via captures of free carriers, the digraph $\mathbf{G}$ represents by itself a NIRC, thereby providing the dependence $U \propto PE^1$. Supposing that at high levels of injection the approximate equality $p \approx n$ is fulfilled, it is possible to write the following asymptotic equality: $U \approx \gamma n$. Further, 48 trees (this number can be found by Kirchhoff's matrix of the digraph $\mathbf{G}$) grow into each vertex of the digraph. However for calculating the coefficient γ it is enough to find only those of them, which the asymptotic values of the tree-weights of the vertices depend on. These trees should contain maximal possible number of the arcs with weights proportional to PE^1 , and they can be found with ease. By four such trees grow into each vertex and weight of each arc for them is just proportional to PE^1 :

$$T_1^{(1)} = (2 \xrightarrow{C_n^{24}n} 4 \xrightarrow{C_p^{43}p} 3 \xrightarrow{C_p^{31}p} 1), \quad (84)$$

$$T_2^{(1)} = (2 \xrightarrow{C_p^{21}p} 1) \& (4 \xrightarrow{C_p^{43}p} 3 \xrightarrow{C_p^{31}p} 1), \quad (85)$$

$$T_3^{(1)} = (4 \xrightarrow{C_p^{42}p} 2 \xrightarrow{C_p^{21}p} 1) \& (3 \xrightarrow{C_p^{31}p} 1), \quad (86)$$

$$T_4^{(1)} = (3 \xrightarrow{C_n^{34}n} 4 \xrightarrow{C_p^{42}p} 2 \xrightarrow{C_p^{21}p} 1), \quad (87)$$

$$T_1^{(2)} = (4 \xrightarrow{C_p^{43}p} 3 \xrightarrow{C_p^{31}p} 1 \xrightarrow{C_n^{12}n} 2), \quad (88)$$

$$T_2^{(2)} = (4 \xrightarrow{C_p^{42}p} 2) \& (3 \xrightarrow{C_p^{31}p} 1 \xrightarrow{C_n^{12}n} 2), \quad (89)$$

$$T_3^{(2)} = (3 \xrightarrow{C_n^{34}n} 4 \xrightarrow{C_p^{42}p} 2) \& (1 \xrightarrow{C_n^{12}n} 2), \quad (90)$$

$$T_4^{(2)} = (1 \xrightarrow{C_n^{13}n} 3 \xrightarrow{C_n^{34}n} 4 \xrightarrow{C_p^{42}p} 2), \quad (91)$$

$$T_1^{(3)} = (1 \xrightarrow{C_n^{12}n} 2 \xrightarrow{C_n^{24}n} 4 \xrightarrow{C_p^{43}p} 3), \quad (92)$$

$$T_2^{(3)} = (1 \xrightarrow{C_n^{13}n} 3) \& (2 \xrightarrow{C_n^{24}n} 4 \xrightarrow{C_p^{43}p} 3), \quad (93)$$

$$T_3^{(3)} = (2 \xrightarrow{C_p^{21}p} 1 \xrightarrow{C_n^{13}n} 3) \& (4 \xrightarrow{C_p^{43}p} 3), \quad (94)$$

$$T_4^{(3)} = (4 \xrightarrow{C_p^{42} p} 2 \xrightarrow{C_p^{21} p} 1 \xrightarrow{C_n^{13} n} 3), \quad (95)$$

$$T_1^{(4)} = (3 \xrightarrow{C_p^{31} p} 1 \xrightarrow{C_n^{12} n} 2 \xrightarrow{C_n^{24} n} 4), \quad (96)$$

$$T_2^{(4)} = (3 \xrightarrow{C_n^{34} n} 4 \xrightarrow{C_n^{12} n} 2 \xrightarrow{C_n^{24} n} 4), \quad (97)$$

$$T_3^{(4)} = (1 \xrightarrow{C_n^{13} n} 3 \xrightarrow{C_n^{34} n} 4 \xrightarrow{C_n^{24} n} 2), \quad (98)$$

$$T_4^{(4)} = (2 \xrightarrow{C_p^{21} p} 1 \xrightarrow{C_n^{13} n} 3 \xrightarrow{C_n^{34} n} 4). \quad (99)$$

Weights of the vertices in an asymptotic limit are:

$$[i] = \sum_{\alpha=1}^4 [T_{\alpha}^{(i)}] = \lambda_i \times n^3, \quad (100)$$

where

$$\begin{aligned} \lambda_1 &= C_n^{24} C_p^{43} C_p^{31} + C_p^{21} C_p^{43} C_p^{31} \\ &\quad + C_p^{42} C_p^{21} C_p^{31} + C_n^{34} C_p^{42} C_p^{21}, \\ \lambda_2 &= C_p^{43} C_p^{31} C_n^{12} + C_p^{42} C_p^{31} C_n^{12} \\ &\quad + C_n^{34} C_p^{42} C_n^{12} + C_n^{13} C_n^{34} C_p^{42}, \\ \lambda_3 &= C_n^{12} C_n^{24} C_p^{43} + C_n^{13} C_n^{24} C_p^{43} \\ &\quad + C_p^{21} C_n^{13} C_p^{43} + C_p^{42} C_p^{21} C_n^{13}, \\ \lambda_4 &= C_p^{31} C_n^{12} C_n^{24} + C_n^{34} C_n^{12} C_n^{24} \\ &\quad + C_n^{13} C_n^{34} C_n^{24} + C_p^{21} C_n^{12} C_n^{34} \end{aligned} \quad (101)$$

and portion of the defects in the i^{th} state ($i = 1, \dots, 4$) proved to be equal to

$$F_i = [i] / \sum_{j=1}^4 [j] = \lambda_i / (\lambda_1 + \lambda_2 + \lambda_3 + \lambda_4). \quad (102)$$

Therefore, the asymptotic rate of GR-transitions is

$$U \approx N_1 C_n^{12} n + N_1 C_n^{13} n + N_2 C_n^{24} n + N_3 C_n^{34} n = \gamma, \quad (103)$$

where

$$\gamma = N_{\text{tot}} \cdot [\lambda_1 (C_n^{12} + C_n^{13}) + \lambda_2 C_n^{24} + \lambda_3 C_n^{34}] / [\lambda_1 + \lambda_2 + \lambda_3 + \lambda_4]. \quad (104)$$

In Fig.11b the other model of DA-pair is shown which differs from the previous model by the transitions $1 \rightarrow 2$ and $2 \rightarrow 1$, as well as $3 \rightarrow 4$ and $4 \rightarrow 3$ due to exchange by an electron only with the conduction band but not with the valence band? So, probabilities of the transitions are: $\omega_2 = C_n^{12} n$, $\omega_{21} = E_n^{21}$, $\omega_{34} = C_n^{34} n$ and $\omega_{43} = E_n^{43}$. The digraph **G** contains now two NIRC's: one of them includes the vertices 1 and 3, which are mutually reachable due to the

transitions $1 \xrightarrow{C_n^{13} n} 3$ and $3 \xrightarrow{C_p^{31} p} 1$, another NIRC holds the vertices 2 and 4, coupled by transitions $2 \xrightarrow{C_n^{24} n} 4$ and $4 \xrightarrow{C_p^{42} p} 2$.

The asymptotic tree-weights of the 2nd and 4th vertices are determined by the following trees respectively:

$$T_1^{(2)} = (4 \xrightarrow{C_p^{42} p} 2) \& (3 \xrightarrow{C_p^{31} p} 1 \xrightarrow{C_n^{12} n} 2), \quad (105)$$

$$T_2^{(2)} = (3 \xrightarrow{C_n^{34} n} 4 \xrightarrow{C_p^{42} p} 2) \& (1 \xrightarrow{C_n^{12} n} 2), \quad (106)$$

$$T_3^{(2)} = (1 \xrightarrow{C_n^{13} n} 3 \xrightarrow{C_n^{34} n} 4 \xrightarrow{C_p^{42} p} 2) \quad (107)$$

and

$$T_1^{(4)} = (3 \xrightarrow{C_p^{31} p} 1 \xrightarrow{C_n^{12} n} 2 \xrightarrow{C_n^{24} n} 4), \quad (108)$$

$$T_2^{(4)} = (3 \xrightarrow{C_n^{34} n} 4) \& (1 \xrightarrow{C_n^{12} n} 2 \xrightarrow{C_n^{24} n} 4), \quad (109)$$

$$T_3^{(4)} = (1 \xrightarrow{C_n^{13} n} 3 \xrightarrow{C_n^{34} n} 4) \& (2 \xrightarrow{C_n^{24} n} 4), \quad (110)$$

so that $[2] = \lambda_2 \times n^3$ and $[4] = \lambda_4 \times n^3$, where $\lambda_2 = C_p^{42} \times (C_p^{31} C_n^{12} + C_n^{34} C_n^{12} + C_n^{13} C_n^{34})$, $\lambda_4 = C_n^{24} \times (C_p^{31} C_n^{12} + C_n^{34} C_n^{12} + C_n^{13} C_n^{34})$. The trees growing into the 1st and 3rd vertices contain not more than two arcs with weights proportional to PE^1 , therefore, $[1] \propto n^2$ and $[3] \propto n^2$. Thus, at high levels of injection the defects will occupy only the 2nd and 4th states: $F_2 = \lambda_2 / (\lambda_2 + \lambda_4) = C_p^{42} / (C_p^{42} + C_n^{24})$, $F_4 = \lambda_4 / (\lambda_2 + \lambda_4) = C_n^{24} / (C_p^{42} + C_n^{24})$, whereas the population of the 1st and 3rd states will decrease in inverse proportion to n . Presence of the ever populated NIRC provides the ensemble of such defects to be non-inertial:

$$U \approx N_2 C_n^{24} n = \gamma, \quad (111)$$

where

$$\gamma = N_{\text{tot}} C_p^{42} C_n^{24} / (C_p^{42} + C_n^{24}). \quad (112)$$

Carrier lifetimes tend to one and the same asymptotic value $\tau_n \approx \tau_p \approx 1/\gamma$, and so do the lifetimes in the previous example.

Let us suppose now that the transitions $2 \leftrightarrow 4$ occur only by electronic exchange with the valence band, but not with the conduction band, so that $\omega_{24} = E_p^{24}$ and $\omega_{42} = C_p^{42} p$.

Corresponding digraph of states **G** in Fig.11c has one NIRC with the vertices 1 and 3. The state $[D^0 A^0]$, which the 2nd vertex corresponds to, is the recombination-passive one, since the defect being in this state cannot capture the injected carriers. Asymptotic magnitude of the tree-weight of the 2nd vertex is determined by the trees

$$T_1^{(2)} = (4 \xrightarrow{C_p^{42} p} 2) \& (3 \xrightarrow{C_p^{31} p} 1 \xrightarrow{C_n^{12} n} 2), \quad (113)$$

$$T_2^{(2)} = (3 \xrightarrow{C_n^{34} n} 4 \xrightarrow{C_p^{42} p} 2) \& (1 \xrightarrow{C_n^{12} n} 2), \quad (114)$$

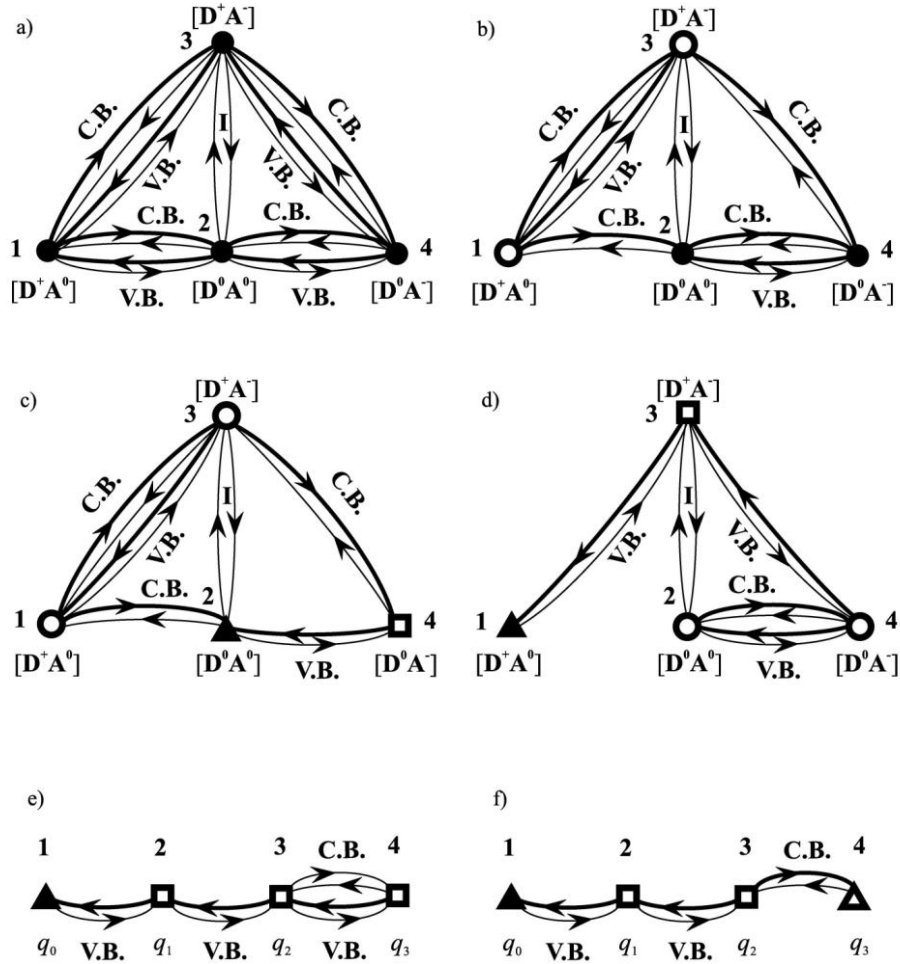


Figure 11. (a) to (d) are the digraphs of states G for a donor-acceptor pair $[DA]$ which can be in four different states. The bipolar injection is supposed. All these models differ by their sets of allowed transitions. A pair of counter arcs marked as "C.B." means the possibility of recharge of the defect due to electronic exchange with the conduction band. The one marked as "V.B." means the transitions with carrier exchange with the valence band. The letter "I" denotes intra-center transitions. Arcs corresponding to capture of charge carriers and having, therefore, the weights proportional to PE^1 , are shown as the bold arrows. Circles show the vertices, which come into some NIRC. The delta circuits are the vertices corresponding to the recombination-passive states. In such states the defect cannot capture the injected carriers. All the remaining states are marked by squares. The solid vertices correspond to the states, whose population does not vanish with increasing the injection level. The remaining states, which become empty in an asymptotical limit, are pictured as empty. (e), (f) The digraphs of states G for four-charge defect without excited states for (e) the hole and (f) bipolar injection

$$T_3^{(2)} = (1 \rightarrow 3 \rightarrow 4 \rightarrow 2). \quad (115)$$

Hence $[2] = \lambda_2 \times n^3$, where $\lambda_2 = C_p^{42} \times (C_p^{31} C_n^{12} + C_n^{34} C_n^{12} + C_n^{13} C_n^{34})$. The trees with maximal weights proportional to n^2 grow into the remaining vertices: for $i = 1, 3$ and $4[i] = \lambda_i \times n^2$, where $\lambda_1 = C_p^{42} \times (E_n^{21} C_n^{34} + E_n^{21} C_p^{31} + \omega_{23} C_p^{31})$, $\lambda_3 = C_p^{42} \times (\omega_{23} C_n^{12} + \omega_{23} C_n^{13} + E_n^{21} C_n^{13})$, $\lambda_4 = \omega_{23} C_n^{13} C_n^{34} + \omega_{23} C_n^{12} C_n^{34} + E_p^{24} C_n^{12} C_n^{34} + E_p^{24} C_n^{13} C_n^{34} + E_n^{21} C_n^{13} C_n^{34} + E_p^{24} C_p^{31} C_n^{12}$. Therefore, in asymptotic limit all defects will be accumulated in the RP-state $F_2 \rightarrow 1$, whereas population of the rest states decreases according to $F_i = \lambda_i / (\lambda_2 \times n)$ ($i = 1, 3, 4$). (116)

The ensemble will be inertial, because the NIRC-states

become devastated with increasing the injection level. Retaining only the major terms in Eq. (83), we find the asymptotic limit of the GR-transition rate:

$$U \approx N_1 C_n^{12} n + N_1 C_n^{13} n + N_3 C_n^{34} n - N_2 E_n^{21} = \gamma, \quad (117)$$

where $\gamma = N_{\text{tot}} \cdot (\lambda_1 C_n^{12} + \lambda_1 C_n^{13} + \lambda_3 C_n^{34} - \lambda_2 E_n^{21}) / \lambda_2$. Such a saturation of the rate U results in linear increase of carrier lifetimes with increasing the injection level: $\tau_n \approx \tau_p \approx n / \gamma$.

In the following example we consider the case when transitions between the states 1 and 2 are forbidden. It means that the donor cannot exchange by carriers with allowed bands whereas the acceptor is neutral. The remaining transitions are shown in Fig. 11d. The digraph G has one NIRC containing the vertices 2 and 4, and one PR-state 1. Having all the trees of maximal weight constructed, we find the asymptotic limits of the tree-weights of all vertices:

$$[1] = \lambda_1 \times n^3, \quad (118)$$

$$[2] = \lambda_2 \times n, \quad (119)$$

$$[3] = \lambda_3 \times n^2, \quad (120)$$

$$[4] = \lambda_4 \times n. \quad (121)$$

Here $\lambda_1 = C_n^{24} C_p^{42} C_p^{31}$, $\lambda_2 = E_p^{13} \times (\omega_{32} C_p^{43} + \omega_{32} C_p^{42} + E_p^{34} C_n^{24})$, $\lambda_3 = E_p^{13} C_n^{24} C_p^{43}$, $\lambda_4 = E_p^{13} C_n^{24} \times (E_p^{34} + \omega_{32})$.

It is seen that population of the “empty” state 1 (without an electron) tends to unity ($F_1 \rightarrow 1$) upon increasing the injection level. Population of the 3rd state decreases as $F_3 = \lambda_3/(\lambda_1 \times n)$, and that of the NIRC-states 2 and 4 wanes in inverse proportion to n^2 : $F_2 = \lambda_2/(\lambda_1 \times n^2)$, $F_4 = \lambda_4/(\lambda_1 \times n^2)$. Limiting value of U is

$$U \approx N_2 C_n^{24} n = \gamma n. \quad (122)$$

Here $\gamma = N_{\text{tot}} \cdot \lambda_2 C_n^{24} / \lambda_1$, i.e. the rate of the GR-transitions becomes in inverse proportion to the number of injected carriers and carrier lifetimes increase proportionally to n^2 : $\tau_n \approx \tau_p \approx n^2 / \gamma$. As mentioned earlier, in this example fastest fading has been reached at bipolar carrier injection for the GR-transition rate through the defects with four states. In case of single polar carrier injection for defects with four states the rate U can wane even faster as PE^2 . Let us show it on an example of the defect with 4-charge and without excited states. Suppose that only holes are injected into the sample, whereas concentration of free electrons remains constant or, maybe, decrease. The corresponding digraph G is shown in Fig. 11e. The defect is “empty” in the 1st state and has one captured electron in the 2nd state. There are two and three captured electrons in the 3rd and 4th states, respectively. It is supposed also that the transitions $1 \leftrightarrow 2$ and $2 \leftrightarrow 3$ occur by electronic exchange only with the valence band. Only the transitions $3 \leftrightarrow 4$ are due to exchange with both of the allowed bands. Since only hole concentration p plays the role of the PE, the digraph G has no NIRC's and the ensemble will certainly be inertial. Only by one tree grows into each vertex determining the asymptotical behaviour of its tree-weight:

$$T_1^{(1)} = (4 \xrightarrow{C_p^{43} p} 3 \xrightarrow{C_p^{32} p} 2 \xrightarrow{C_p^{21} p} 1), \quad (123)$$

$$T_1^{(2)} = (1 \xrightarrow{E_p^{12}} 2) \& (4 \xrightarrow{C_p^{43} p} 3 \xrightarrow{C_p^{32} p} 2), \quad (124)$$

$$T_1^{(3)} = (1 \xrightarrow{E_p^{12}} 2 \xrightarrow{E_p^{23}} 3) \& (4 \xrightarrow{C_p^{43} p} 3), \quad (125)$$

$$T_1^{(4)} = (1 \xrightarrow{E_p^{12}} 2 \xrightarrow{E_p^{23}} 3 \xrightarrow{C_n^{34} n + E_p^{34}} 4), \quad (126)$$

so that

$$[1] = \lambda_1 \times p^3, \quad (127)$$

$$[2] = \lambda_2 \times p^2, \quad (128)$$

$$[3] = \lambda_3 \times p, \quad (129)$$

$$[4] = \lambda_4, \quad (130)$$

where $\lambda_1 = C_p^{43} C_p^{32} C_p^{21}$, $\lambda_2 = E_p^{12} C_p^{43} C_p^{32}$, $\lambda_3 = E_p^{12} E_p^{23} C_p^{43}$, $\lambda_4 = E_p^{12} E_p^{23} (C_n^{34} n + E_p^{34})$. With increasing the hole concentration more and more defects will occupy the “empty” RP-state,

$$F_1 \xrightarrow{p \rightarrow \infty} 1 \quad (131)$$

whereas population of the remaining states decrease as:

$$F_2 = \lambda_2/(\lambda_1 \times p), \quad (132)$$

$$F_3 = \lambda_3/(\lambda_1 \times p^2), \quad (133)$$

$$F_4 = \lambda_4/(\lambda_1 \times p^3). \quad (134)$$

In asymptotical limit the equation for the rate of GR-transitions looks like

$$U \approx N_3 C_n^{34} n = \gamma p^2, \quad (135)$$

where $\gamma = N_{\text{tot}} \cdot (\lambda_3 C_n^{34} n) / \lambda_1$, i.e. U drops in inverse proportion to p^2 . Thus lifetime of electrons and holes increase as p^2 : $\tau_n \approx (n/\gamma) p^2$ and $\tau_p \approx p^3/\gamma$, respectively.

Finally, 4-vertex digraph of states G is shown in Fig. 11f, which corresponds to the defects with recombination rate U , equalling to zero at any injection conditions. Indeed, the

digraph G contains three cycles: $\tilde{C}_1=1 \xrightarrow{E_p^{12}; 0} 2 \xrightarrow{C_p^{21} p; 0} 1$, $\tilde{C}_2=2 \xrightarrow{E_p^{23}; 0} 3 \xrightarrow{C_p^{32} p; 0} 2$ and $\tilde{C}_3=3 \xrightarrow{C_n^{34} n; -1} 4 \xrightarrow{E_n^{43}; +1} 3$. In the above notations the arrows are the transition probabilities $\omega_{ij}^{(\alpha)}$ and the change of number of electrons in the conduction band $\nu_{ij}^{(\alpha)}$ is caused by this transition. Net change of number of free electrons along each cycle turns out to be equal to zero: $\tilde{V}_1 = \tilde{V}_2 = \tilde{V}_3 = 0$, that is why $U=0$ (see, e.g., Eq.(50)).

5. Analysis and Discussion

It should be noted that importance of the graph theory is much wider than being considered as one of the methods of studying the GR processes in semiconductors through point defects. The theory can be applied to any point defects with many numbers of states and with complicated transitions between them. The defects should be independent each from other and their kinetics should be possible to study by kinetic equations. Discrete approximation with any control-lable accuracy can be applied for many systems with continuous spectra of states. Examples of such systems are, e.g., extended defects, which can be described by the kinetic equations of Pauli, or Kolmogorov-Fokker-Planck equations, or integro-differential equation by Kolmogorov and Feller, accounting both continuous and abrupt change of the state of the system. This means that the distribution function and the rate of the GR processes for some extended defects with continuous spectra of states can also be built in the form of tree-weight rule similar to the discrete systems described by Eqs. (29)-(32). In such case, weights of the states should be calculated not by summation, but by integration over all oriented rooted spanning trees, entirely covering the strongly connected sink components of the continuous phase space. Here the integration over the oriented tree should be taken symbolically as a kind of limit that is associated with

division of the phase space into small size cells, and in this respect, the integration along oriented tree is similar to the representation of the Feynman path integrals. These analyses indicate that the tree form of the state weights is the natural and inherent feature of any conservative linear system in steady state conditions, regardless of the features of the scheme allowed transitions, or features and the number of possible states of the system. By other words, it is the natural property of such systems. Knowledge of it allows to build the schemes of analysis of systems, which uses tree property of the weights of states.

6. Conclusions

In the paper we have studied GR processes through point defects by the graph theory. In the theory the defect states will be indicated by dots whereas transitions between them as arcs. We show that in the description of the GR processes through point defects by the graph theory the principle of detailed balance can be accounted for by simultaneous including into consideration of both direct and reverse transitions between the defect states i and j ($j \rightarrow i$ and $j \leftarrow i$). We have classified defect models within the definitions of the graph theory and discussed why the theory present interest in the study of the GR processes. We found the equation for the stationary distribution function of the recombination centers on their states, which is universal for all point defects. We show that the equation can be derived without constructing the system of kinetic equations for the defect states and without solving the system of equations as it was done before by using the kinetic theory. We demonstrate that to find the distribution function of defects on their states it is sufficient to construct the set of rooted trees covering the digraph of states of defects G . We found that the graph theory can be supplementary to the kinetic theory by contributing to simplification of the model of the defects. If in the kinetic theory such a simplification is based on neglecting the defect transitions with smallest probability, by using the graph theory we demonstrate that it should be based not only on this, but also on strategic importance of the transition in the digraph of states of the defect. Also, we show that the graph theory can be efficient to find the equation for the distribution function of the defect on its states at asymptotic level corresponding to high injection level or temperature. It is based on dependence of the distribution function of defects on relatively small number of oriented trees of maximal weight, which can easily be determined by the methods of the graph theory. For that aim some transitions of the defect not included into any of the maximal trees determining asymptotical behaviour of the distribution function should be excluded from consideration. The distribution function itself can be very sensitive to some transitions of small probabilities included into maximal trees, but can be insensitive to other transitions with much greater probabilities and not included into the maximal trees. In

graph theory this point is related to the concept of structural stability of dynamic systems.

We show that the graph theory allows to construct the equation for the rate of GR processes. We have derived such an equation just using the digraph of states G and without solving the system of kinetic equations. Distinct from already existing equations for the rate of GR processes, which work for particular type of the model of recombination, it is universal and works for all kinds of point defects. We show that such an equation can be derived without designing the system of kinetic equations and for that preliminary knowledge or derivation of distribution of defects on states for finding the equation for U is not needed. The rate U contains some terms, which are universal for all point defects and it allows the approximation $U = \Delta n(\Delta p) / \tau_{n,p}$, where $\Delta n(\Delta p)$ and $\tau_{n,p}$ are the excess electron(hole) concentration and lifetime. Based on the equation the rate of GR rate has been derived for some models of recombination via single level defects, excitonic states, bistable defects, and donor acceptor pairs.

We show that the graph theory is efficient in formulation and solution of a wide range of challenges related to GR processes. We found the possibility of static influence of defects on GR processes without changing the charge state of the defect. It can take place together with the conventional astatic ones. We have revisited the problem of inertiality of recombination centers. In previous studies inertiality of recombination centers has been ascribed to number of energy levels of the centers, which is assumed to be more than one. Then delay in the GR processes could take place because of carrier exchange between the energy levels of defects. Here we have introduced different model of inertiality of the processes. We show that asymptotical dependence of U on carrier density at high injection levels can be found, whereas in the traditional approach it would be hardly possible to find so convenient criteria of lack of inertia. This work is the first attempt of systematic exposition of application of the graph theory in the study of GR processes considered mainly for point defects and it shows that the theory together with the kinetic approach is a new tool for investigation of GR processes.

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Appendix A

Let us deduce the Eqs.(12)-(15), which are on the base of the tree-weight rule from the matrix-tree theorem[1]. If the normalization condition for the distribution function has not been taken into consideration, then the components F_i ($i=1, \dots, M$), in accordance with Eqs.(3)-(4), obey to the system of linear homogeneous equations

$$\mathbf{W}\mathbf{F} = \mathbf{0} \quad (\text{A1})$$

with (M×M) matrix of coefficients $\mathbf{W} = \|w_{ij}\|$. Off-diagonal elements w_{ij} of the matrix is equal to the probabilities ω_{ij} of transitions $j \rightarrow i$.

$$w_{ij} = \omega_{ij} \quad \text{if } i \neq j, \quad (\text{A2})$$

The diagonal elements w_{ii} are equal to the sum of probabilities of all transitions from the state i into the other states taken with minus sign, i.e.: $w_{ii} = -\sum_{j \neq i} \omega_{ij}$. Thus,

all off-diagonal elements of the $\mathbf{W}$ -matrix are nonnegative, and the sum of all elements in any column is zero:

$$(w_{ij} \geq 0 \quad \text{if } i \neq j) \quad \text{and} \quad \sum_{i=1}^M w_{ij} = 0 \quad (j = 1, \dots, M). \quad (\text{A3})$$

From (A3) one can get the following properties of the $\mathbf{W}$ -matrix:

1) The $\mathbf{W}$ -matrix is degenerated, i.e. $\text{rank } \mathbf{W} \leq M-1$ and $\det \mathbf{W} = 0$;

2) all elements of the $\mathbf{W}$ -matrix in the same column have identical cofactors, i.e. the cofactors W_{ij} of the elements w_{ij} are actually independent of the row index:

$$W_{1j} = W_{2j} = \dots = W_{Mj} = W(j) \quad (j = 1, \dots, M); \quad (\text{A4})$$

3) all non-zero cofactors $W(j)$ have the same sign. Namely, if M is even then all of the cofactors are negative and otherwise they are positive;

4) if rank of the $\mathbf{W}$ -matrix is equal to the largest possible value ($M-1$), i.e. if at least one of the cofactors $W(j)$ is not equal to zero, then in this (and only this) case any of ($M-1$) rows of the $\mathbf{W}$ -matrix will be linearly independent.

Let us assume for a while, that the requirement 4) is fulfilled, which says that any equation of the system (A1) can be derived from the rest ones. In such case instead of using an arbitrary, say, the l -th equation one can use the normalization of distribution function to unity. Thus one can obtain the inhomogeneous set of equations

$$\mathbf{B}\mathbf{F} = \mathbf{e}_1 \quad (\text{A5})$$

with (M×M) matrix $\mathbf{B} = \|b_{ij}\|$, which has only unities in the l -th row and coincides with the $\mathbf{W}$ -matrix in rest ones. All components of the column-vector $\mathbf{e}_1$ except the l -th one, which is equal to unity, are equal to zero. Then using the Kronecker delta it is possible to write down $(\mathbf{e}_1)_i = \delta_{il}$. Let us calculate the determinant of the $\mathbf{B}$ -matrix by

decomposing it by the l -th row: $\det \mathbf{B} = \sum_{j=1}^M b_{lj} B_{lj} =$

$$\sum_{j=1}^M 1 \cdot W_{lj} = \sum_{j=1}^M W(j), \quad \text{and using equality of the}$$

cofactors B_{lj} and W_{lj} of elements of the l -th row b_{lj} and w_{lj} . Since among the magnitudes of $W(j)$ there are non-zero ones and all of them, in accordance with the property 3), are of one sign, then $\det \mathbf{B} \neq 0$ and the set of equations (A5) can be

solvable:

$$F_i = (\mathbf{B}^{-1} \mathbf{e}_1)_i = (\mathbf{B}^{-1})_{il} = \frac{B_{li}}{\det \mathbf{B}} = \frac{W(i)}{\sum_{j=1}^M W(j)} = \frac{|W(i)|}{\sum_{j=1}^M |W(j)|}, \quad (i = 1, \dots, M). \quad (\text{A6})$$

Therefore, one obtains the weight rule, in which the absolute value of the cofactor $|W(i)|$ plays the role of the “kinetic weight” of the i -th state. Further, suppose that the system is described by the M -vertex digraph of states $\mathbf{G}$. Kirchhoff's matrix $\mathbf{K}(\mathbf{G})$ of the digraph $\mathbf{G}$ is the (M×M)-matrix with i -th diagonal element k_{ii} equal to the sum of the weights of all the arcs coming into the vertex i . The off-diagonal element k_{ij} ($i \neq j$) is equal to the sum (with minus sign) of the weights of all arcs issuing from the vertex j into the vertex i (see Ref.[1]). From this definition, in particular, it follows that all elements of the same row of the Kirchhoff's matrix have identical cofactor. Let $K_i(\mathbf{G})$ be a cofactor of the elements of the i -th row. According to the matrix-tree theorem, $K_i(\mathbf{G})$ is equal to the total weight of all spanning trees, growing out of the vertex i . Proof of the theorem has been reported in Ref.[1, 2]:

$$K_i(\mathbf{G}) = \sum_{\alpha} [T_{\alpha}^{(i)}]. \quad (\text{A7})$$

The stroke in the notation $T_{\alpha}^{(i)}$ of the tree growing out of the vertex i serves to distinguish it from the tree $T_{\alpha}^{(i)}$ growing into the vertex i . Weight of the growing out tree $T_{\alpha}^{(i)}$, as well as the one of the growing into tree, is equal to the product of weights of all arcs included into it: $[T_{\alpha}^{(i)}] \equiv$

$\prod_{j \rightarrow k \in T_{\alpha}^{(i)}} \omega_{jk}$. Let us note now that the $\mathbf{W}$ -matrix and the

Kirchhoff's matrix $\mathbf{K}(\mathbf{G})$ are related with each other as:

$$\mathbf{W} = -(\Re \mathbf{K}(\mathbf{G}))^T. \quad (\text{A8})$$

Here the superscript “T” means transposition, and the operation $\Re$ means interchange of the indices of initial i and final j states in the weights of all arcs ω_{ij} . For example, $\Re(\omega_{32} \times \omega_{12}) = \omega_{23} \times \omega_{21}$. Note also that all these conversions, i.e., multiplication by (-1) , transposition and interchanging of indices, are possible to perform in the arbitrary order. It follows from Eq. (A8) that between the cofactors $W(i)$ and $K_i(\mathbf{G})$ of elements of the i -th column of the $\mathbf{W}$ -matrix and the i -th row of Kirchhoff's matrix there is also the following relationship: $W(i) = (-1)^{M-1} \Re K_i(\mathbf{G})$. Using the Eq.(A7) one can obtain $|W(i)| = |\Re K_i(\mathbf{G})| = |\Re(\sum_{\alpha} [T_{\alpha}^{(i)}])| =$

$|\sum_{\alpha} [\Re T_{\alpha}^{(i)}]| = \sum_{\alpha} [T_{\alpha}^{(i)}] = [i]$. Here we have taken into

account that as a result of the operation $\Re$, which changes orientation of all arcs into opposite ones, every tree $T_{\alpha}^{(i)}$ growing out of a vertex i turns into the tree $T_{\alpha}^{(i)}$ growing into the vertex i . Thus, the kinetic weight $|W(i)|$ of the i -th state in Eq. (A6) coincides with the tree-weight $[i]$ of the i -th

vertex of a digraph of states $\mathbf{G}$ defined in Eqs. (12) and (13), and one gets the tree-weight rule Eqs. (12)-(15).

It should be noted that upon deriving the Eq. (A6) it is supposed that at least one of the cofactors $W(i)$ is not equal to zero. By virtue of the equality $|W(i)| = [i]$ it means that the digraph $\mathbf{G}$ should have at least one “growing into” type of tree covering the digraph. Then the tree-weight of its root vertex will be different from zero. Also, it is equivalent to that in the digraph $\mathbf{G}$. There should be at least one vertex accessible for all remaining ones. Only such a vertex can be a root for a tree [1]. For this purpose it is necessary and sufficient that the digraph $\mathbf{G}$ has only one strong component of sink type. Indeed, from the graph theory it is known that any digraph $\mathbf{G}$ has at least one strong component and each vertex of $\mathbf{G}$ belongs to the components. There are three types of strong components: (i) sink components denoted by $\mathbf{A}$. It is possible to come into $\mathbf{A}$ and to leave it; (ii) source components ($\mathbf{R}$). It is possible to leave $\mathbf{R}$ but it is impossible to come into it; transit components ($\mathbf{T}$). It is possible to do both to come into $\mathbf{T}$ and to go out of it.

Note that visual representation of possible transitions between strong components of a digraph $\mathbf{G}$ is provided by its condensation $\mathbf{G}^*$ [3]. Any digraph $\mathbf{G}$ has one $\mathbf{A}$ -component, and if this component is unique, then each of its vertex will be accessible from any other vertex of the digraph $\mathbf{G}$. Thus, starting from any vertex of the $\mathbf{R}$ -component, it is possible to pass through the vertices in $\mathbf{T}$ -components and to come back to the $\mathbf{A}$ -component, reaching there any vertex that is well visible on the example of the digraph shown in Fig. 11a. In this case each vertex of the $\mathbf{A}$ -component will be a root of at least one tree covering $\mathbf{G}$. If number of the $\mathbf{A}$ -components is ≥ 2 , then the vertices belonging to different $\mathbf{A}$ -components will be unreachable for each other, since there are no arcs outgoing from the $\mathbf{A}$ -components. Therefore, there will be no such vertices in $\mathbf{G}$, which would be accessible from all others (see, for example, Fig. 11a) and no trees covering $\mathbf{G}$. As discussed above, in this case the tree-weight rule is still valid but it should be applied not to the particular digraph $\mathbf{G}$ as a whole, but to each of its $\mathbf{A}$ -components separately, so that the rule takes on the form of Eqs. (29)-(32).

It is also useful to analyse the above result from the other point of view of improving of understanding the question as to how the tree-construction of a vertex weight works. We want to show that only the weights defined by this way will provide the balance between the rates of the defects coming into any of their states and going out from the states at arbitrary variations of probabilities of transitions. Such a balance is necessary for achieving the steady state of the system. Solution of the set of Eqs.(3)-(4) expressing the balance must have the form of the tree-weight rule described by the Eqs. (12)-(15).

First of all, we shall give some information about functional digraphs (see also Refs.^{1,2}). A functional digraph (to be called hereafter as Φ -digraph) represents a cycle $\mathbf{C}$. Some trees, forming the so-called “forest”, may grow into the vertices of the cycle. Characteristic feature of a Φ -digraph is that exactly one arc outgoes from each of its vertex. If a

tree growing into the vertex i will be added with an arc connecting the root vertex i with itself or with any other vertex j one gets a Φ -digraph and vice versa. The new arc will close a cycle $\mathbf{C}$ so that the root vertex i will appear in this cycle. The arcs, which have not been included into a cycle, generate the forest growing into the cycle. If an arc of a cycle $\mathbf{C}$ of a Φ -digraph has been excluded then one can get a tree growing into the vertex, which the removed arc was coming from. If a Φ -digraph contains all vertices and arcs of a digraph $\mathbf{G}$, then one can say that the Φ -digraph covers $\mathbf{G}$. Any strong digraph $\mathbf{G}$ can be covered with at least one Φ -digraph. Let us describe now two ways of constructing of all Φ -digraphs covering $\mathbf{G}$ and containing some fixed vertex i in their cycles $\mathbf{C}$.

First way. If a set of all trees $\{T_{a_i}^{(i)}\}$ covering $\mathbf{G}$ and growing into the vertex i is created, then each of them in turn without repetitions is combined with one of the arcs $i \rightarrow j$ coming from the i -th vertex. As a result of each such association, one of the required Φ -digraphs will be gained, and in the end one can bust all the Φ -digraphs by one time each. It follows from the procedure that the total weight of the Φ -digraphs will be equal to $\sum_{j \neq i} \sum_{\alpha_i} \omega_{ij} [T_{a_i}^{(i)}]$, or

$(\sum_{j \neq i} \omega_{ij}) \cdot (\sum_{\alpha_i} [T_{a_i}^{(i)}])$. Weight of a Φ -digraph is equal to the product of the weights of all arcs included into it. This is the reason why the weight of the digraph can be presented as product of the weights of the trees included into it $[T_{a_i}^{(i)}]$ by the weight ω_{ij} of an arc which is issued from the i th vertex.

Second way. For all vertices j , distinct from i , and bound with it with an arc $j \rightarrow i$, the sets of all trees $\{T_{a_j}^{(j)}\}$ is created growing into them and covering $\mathbf{G}$. Then each tree is supplemented with the arc $j \rightarrow i$ which outgoes from its root j and comes into the vertex i . In the end one can again get the same set of Φ -digraphs. Such a way of construction allows one to write down total weight of the digraphs as $\sum_{j \neq i} \sum_{\alpha_j} \omega_{ji} [T_{a_j}^{(j)}]$, or $\sum_{j \neq i} (\omega_{ji} \cdot \sum_{\alpha_j} [T_{a_j}^{(j)}])$. Since in both of the above ways one gets the same result, it is possible to write down the following topological identity, which follows from properties of the spanning rooted trees:

$$(\sum_{j \neq i} \omega_{ij}) \cdot (\sum_{\alpha_i} [T_{a_i}^{(i)}]) \equiv \sum_{j \neq i} (\omega_{ji} \cdot \sum_{\alpha_j} [T_{a_j}^{(j)}]) \quad (i=1, \dots, M). \quad (\text{A9})$$

Note that the Equation is still valid in the case when there are no arcs going out from the i -th vertex ($\omega_{ij} = 0$). Then the left-hand side of Eq. (A9) becomes equal to zero and the right hand side will be equal to zero just because of absence of spanning trees growing into the vertex j other than i . Thus, the tree-weight $[i] \equiv \sum_{\alpha_i} [T_{a_i}^{(i)}]$ defined in Eqs. (12) and (4) provides automatically the equality of rates of transitions of

defects from and into the state i :

$$\left(\sum_{j \neq i} \omega_{ij}\right) \cdot [i] = \sum_{j \neq i} \omega_{ji} \cdot [j] \quad (i = 1, \dots, M). \quad (\text{A } 10)$$

Namely, each addend on the left-hand side of the above Eq. corresponds to the same addend on the right hand. By other words, the tree-weights $[i]$ turn the set of equations (A1) into identities, which are valid for arbitrary magnitudes of probabilities ω_{ij} , and hence they can always be taken as its solution. As it was shown above, for a strong digraph G and in general, for any digraph with only one strong sink component the rank of the system (A1) gets the largest possible magnitude $M-1$. Then, as is known from the theory of linear equations, any solution of the system (A1) may differ from $[i]$ only by some factor C : $F_i = C \cdot [i]$ ($i = 1, \dots, M$), and the normalization conditions of distribution function to unity finally leads to Eqs.(14) and (15).

Appendix B

Let us prove the equality $U_n = U_p$ at steady state conditions. For this purpose we shall make a difference of the rates U_n and U_p , which is equal to $U_n - U_p = \sum_{i,j} N_i \omega_{ij} \Delta l_{ij} =$

$\sum_{i,j} N_i \omega_{ij} l_j - \sum_{i,j} N_i \omega_{ij} l_i$ [Eqs. (39),(40)]. Further, we interchange the indexes $i \leftrightarrow j$ in the first sum:

$$\begin{aligned} \sum_{i,j} N_j \omega_{ji} l_i - \sum_{i,j} N_i \omega_{ij} l_i &= \sum_{i,j} (N_j \omega_{ji} - N_i \omega_{ij}) \cdot l_i \\ &= \sum_i \left[-\left(\sum_j \omega_{ij}\right) N_i + \sum_j N_j \omega_{ji} \right] \cdot l_i. \end{aligned} \quad (\text{B1})$$

The equation in the square brackets is the difference between the rate of transition of the defects into the i -th state from all other states and outgoing rate from the state. This will give the resulting rate of temporal change of number of defects in the i -th state $\dot{N}_i$. Thus, $U_n - U_p = \sum_i \dot{N}_i l_i$. It

expresses the evident result that the difference between the capture rate of conduction electrons (holes) into the defects $U_n (U_p)$ is equal to the rate of change of total number of electrons bound on the defects. In the steady state conditions $\dot{N}_i = 0$ for all $i = 1, \dots, M$. Hence $U_n = U_p$.

Appendix C

We shall deduce the equation for the rate of GR-transitions [Eq. (46)] by using the Eq. (38). For this purpose we shall write the density of defects N_i in the i -th state via the tree-weights of the vertices of the digraph of states G : $N_i = N_{\text{tot}} \cdot [i] / \sum_{j=1}^M [j]$. Here the tree-weight $[i]$ is obtained by summing the weights of all the trees covering G and growing into the i -th vertex: $[i] = \sum_{\alpha} [T_{\alpha}^{(i)}]$. Thus, the

Eqs. (39) and (40) become

$$U = N_{\text{tot}} \cdot \frac{- \sum_{i,j} \sum_{\alpha} [T_{\alpha}^{(i)}] \omega_{ij} v_{ij}}{\sum_{j=1}^M [j]}. \quad (\text{C1})$$

As mentioned above, association of the tree $T_{\alpha}^{(i)}$ growing into the i -th vertex with an arc $i \rightarrow j$ issued from its root vertex i gives some Φ -graph Φ_k covering G and that the product $[T_{\alpha}^{(i)}] \cdot \omega_{ij}$ gives the weight $[\Phi_k]$ of this Φ -graph. Note that adding the arc $i \rightarrow j$ closes the cycle C_k together with remaining arcs of the tree $T_{\alpha}^{(i)}$, not included into this cycle, constitute the Φ -graph Φ_k . Thus, each addend in the numerator of the fraction (C1) represents product (taken with minus sign) of the weight of some Φ -graph Φ_k by the change of the number of free electrons corresponding to some arc belonging to its cycle C_k . Since the summation in the numerator of eq.(C1) is carried out over *all* trees, and since for each of them *all* possible variants of association with the arc are considered, then it will contain the weights of all Φ -graphs covering G . It is easy to understand that the weight of each Φ -graph Φ_k will meet as many times as many arcs are there in its cycle C_k , and every time it will be multiplied by the number v_{ij} corresponding to the next arc of the cycle. Combining the addends with one and the same weight $[\Phi_k]$ together, one can get the factor v_k , which is equal to the net change of the number of free electrons along the cycle C_k of the Φ -graph Φ_k and we obtain the Eq. (46).

Appendix D

Let us show that in the absence of degeneracy, the rate of GR-transitions can be calculated by the Eq. (51) provided that the model together with each transition holds its reverse transition. Let the probability $\omega_{ij}^{(\alpha)}$ of transition of a defect from the i -th state into the j -th state by some particular mechanism *axis* $T_{\alpha}^{ij} n^{\xi_{ij}^{(\alpha)}} p^{\zeta_{ij}^{(\alpha)}}$. As is known, in absence of degeneracy the exponents $\xi_{ij}^{(\alpha)}$ and $\zeta_{ij}^{(\alpha)}$ coincide with number of free electrons and holes involved in the transition, respectively. As a result of the transition, number of free electrons varies by $v_{ij}^{(\alpha)}$. In accordance with Eq. (51), number of holes will be varied by $\pi_{ij}^{(\alpha)} = \Delta l_{ij} + v_{ij}^{(\alpha)}$. Note that the number of free electrons $\xi_{ij}^{(\alpha)}$ participating in the transition and the change of $\xi_{ij}^{(\alpha)}$ in the conduction band $v_{ij}^{(\alpha)}$ due to the transition not necessarily should coincide with each other. Another example is the Auger-process

shown in Fig.7c, in which one free electron participates: $\xi_{ij}^{(\alpha)} = 1$, but the number of conduction electrons does not vary: $\nu_{ij}^{(\alpha)} = 0$. The same concerns to the quantities $\zeta_{ij}^{(\alpha)}$ and $\pi_{ij}^{(\alpha)}$. Transition probability of a defect from the j^{th} state into the i^{th} state by the reverse mechanism $\bar{\alpha}$ will be

$$\begin{aligned} \omega_{ji}^{(\bar{\alpha})} &= T_{\bar{\alpha}}^{ji} n^{\xi_{ji}^{(\bar{\alpha})}} p^{\zeta_{ji}^{(\bar{\alpha})}} = T_{\bar{\alpha}}^{ji} n^{\xi_{ij}^{(\alpha)} + \nu_{ij}^{(\alpha)}} p^{\zeta_{ij}^{(\alpha)} + \pi_{ij}^{(\alpha)}} = \\ &= (T_{\bar{\alpha}}^{ji} / T_{\alpha}^{ij}) n^{\nu_{ij}^{(\alpha)}} p^{\pi_{ij}^{(\alpha)}} \cdot \omega_{ij}^{(\alpha)} = \\ &= (T_{\bar{\alpha}}^{ji} / T_{\alpha}^{ij}) (np / n_i^2)^{\nu_{ij}^{(\alpha)}} p^{\Delta_{ij}} \cdot \omega_{ij}^{(\alpha)}. \end{aligned} \quad (D1)$$

Here we took into account the fact that as a result of the transition by the α -mechanism number of free electrons and holes becomes equal to $\xi_{ij}^{(\alpha)} + \nu_{ij}^{(\alpha)}$ and $\zeta_{ij}^{(\alpha)} + \pi_{ij}^{(\alpha)}$ respectively, and it will be the initial parameter for the reverse transition by the $\bar{\alpha}$ -mechanism. The ratio of the coefficients $T_{\bar{\alpha}}^{ji} / T_{\alpha}^{ij}$ can be found from the principle of detailed balance: since in equilibrium the rates of transitions by mutually reverse mechanisms equilibrate each other, i.e.

$$(N_i)_{eq} \cdot (\omega_{ij}^{(\alpha)})_{eq} = (N_j)_{eq} \cdot (\omega_{ji}^{(\bar{\alpha})})_{eq}. \quad (D2)$$

Then

$$T_{\bar{\alpha}}^{ji} / T_{\alpha}^{ij} = \frac{(N_i / N_j)_{eq}}{(n_i)^{2 \cdot \nu_{ij}^{(\alpha)}} \cdot (p_0)^{\Delta_{ij}}}. \quad (D3)$$

Here n_i is the intrinsic concentration of electrons, p_0 is the equilibrium concentration of holes, and the ratio of the equilibrium concentrations of defects $(N_i / N_j)_{eq}$ is determined according to Gibbs statistics. Thus, in a non-degenerate material there is the following correlation between probabilities of transitions by mutually reverse mechanisms:

$$\omega_{ji}^{(\bar{\alpha})} = (N_i / N_j)_{eq} \cdot (np / n_i^2)^{\nu_{ij}^{(\alpha)}} \cdot (p / p_0)^{\Delta_{ij}} \cdot \omega_{ij}^{(\alpha)}. \quad (D4)$$

Let us now consider the arbitrary cycle $\tilde{C}_k^{\mu} = i_1 \rightarrow i_2^{(\alpha_1)} \rightarrow \dots \rightarrow i_{N-1}^{(\alpha_{N-2})} \rightarrow i_N^{(\alpha_{N-1})} \rightarrow i_1^{(\alpha_N)}$ passing through N different vertices $i_1, i_2, \dots, i_{N-1}, i_N$, with arcs $\alpha_1, \alpha_2, \dots, \alpha_N$ corresponding to different mechanisms. As discussed above, the cycle belongs to the k^{th} subgroup of cycles passing through the vertices in certain order and differing each from other by choice of the multiple arcs, i.e. by the mechanisms of transitions, and in this subgroup it will be characterized the number μ . Its weight will be equal to $[\tilde{C}_k^{\mu}] = \omega_{i_1 i_2}^{(\alpha_1)} \cdot \omega_{i_2 i_3}^{(\alpha_2)} \cdot \dots \cdot \omega_{i_{N-1} i_N}^{(\alpha_{N-1})} \cdot \omega_{i_N i_1}^{(\alpha_N)}$. Since each transition comes with the reverse one, the digraph G contains another cycle $\tilde{C}_k^{\mu'} = i_1 \leftarrow i_2^{(\bar{\alpha}_1)} \leftarrow \dots \leftarrow i_{N-1}^{(\bar{\alpha}_{N-2})} \leftarrow i_N^{(\bar{\alpha}_{N-1})} \leftarrow i_1^{(\bar{\alpha}_N)}$, which will pass through the same vertices as $\tilde{C}_k^{\mu}$, but in the opposite direction corresponding to reverse mechanisms of transition.

The cycle will belong to the group k' and will have the number μ' . By using the Eq. (D1) one can find the relation between the weights of the two mutually reverse cycles $\tilde{C}_k^{\mu}$ and $\tilde{C}_k^{\mu'}$: $[\tilde{C}_k^{\mu'}] = \omega_{i_2 i_1}^{(\bar{\alpha}_1)} \cdot \omega_{i_3 i_2}^{(\bar{\alpha}_2)} \cdot \dots \cdot \omega_{i_N i_{N-1}}^{(\bar{\alpha}_{N-1})} \cdot \omega_{i_1 i_N}^{(\bar{\alpha}_N)} = (np / n_i^2)^{\tilde{\nu}_k^{\mu}} \cdot [\tilde{C}_k^{\mu}]$. Here $\tilde{\nu}_k^{\mu}$ is the total change of number of the free electrons along with the cycle $\tilde{C}_k^{\mu}$ because upon cyclic multiplication both $(N_i / N_j)_{eq}$ and $(p / p_0)^{\Delta_{ij}}$ equals to 1, and degree in the power of the equation $(np / n_i^2)^{\nu_{ij}^{(\alpha)}}$, being added will equal to $\tilde{\nu}_k^{\mu}$. At the same time it is evident that change of number of electrons in the conduction band occurring in the mutually reverse cycles are opposite as well $\tilde{\nu}_k^{\mu'} = -\tilde{\nu}_k^{\mu}$, because they contain the mutually reverse mechanisms. Therefore the net contribution from the two mutually reverse cycles to the numerator of the Eq.(50) will be equal to $\tilde{\nu}_k^{\mu} [\tilde{C}_k^{\mu}] + \tilde{\nu}_k^{\mu'} [\tilde{C}_k^{\mu'}] = (1 - (np / n_i^2)^{\tilde{\nu}_k^{\mu}}) \times \tilde{\nu}_k^{\mu} [\tilde{C}_k^{\mu}]$. If $\tilde{\nu}_k^{\mu} > 0$, then it

can be represented as $(1 - (np / n_i^2)) \times \left\{ \sum_{m=0}^{\tilde{\nu}_k^{\mu}-1} (np / n_i^2)^m \right\} \times \tilde{\nu}_k^{\mu} [\tilde{C}_k^{\mu}]$. Then the Eq. (50) becomes of the form of Eq.(51).

Appendix E

Upon proving equality of the rate of GR-transitions U_{eq} to zero at equilibrium one should bear in mind that the digraph of states G describing the system must be symmetrical. Then the principle of detailed balance will be fulfilled, which requires that a reverse transition for each of the direct transition. Since a symmetrical digraph G with a cycle C_k always contains a counter cycle $\bar{C}_k$, which passes through the same vertices as C_k , but in the opposite directions, all cycles of such a digraph can be divided into pairs of mutually reverse cycles. For this reason all Φ -graphs covering G can be divided into pairs Φ_k and $\bar{\Phi}_k$, which will differ each from other only by orientation of their cycles. However, these cycles will have the same sets of trees growing into them. In equilibrium state weights of the mutually reverse cycles are equal, which follows from the principle of detailed balance:

$$\begin{aligned} [C_k]_{eq} &= \prod_{i \rightarrow j \in C_k} (\omega_{ij})_{eq} = \prod_{j \rightarrow i \in \bar{C}_k} (N_j / N_i)_{eq} \times (\omega_{ji})_{eq} = \\ &= \prod_{j \rightarrow i \in \bar{C}_k} (\omega_{ji})_{eq} = [\bar{C}_k]_{eq}. \end{aligned} \quad (E1)$$

Cyclic product of the fractions $(N_j / N_i)_{eq}$ is equal to unity.

Therefore, the equilibrium weights of the conjugate Φ -graphs will be equal $[\Phi_k]_{eq} = [\bar{\Phi}_k]_{eq}$ whereas changes of the numbers of free carriers along the cycles C_k and $\bar{C}_k$ will be opposite $(v_k)_{eq} = -(\bar{v}_k)_{eq}$. Indeed, the mutually conjugate cycles C_k and $\bar{C}_k$ include the mutually reverse mechanisms of transitions α and $\bar{\alpha}$ which cause the opposite changes in number of free carriers in allowed bands: $v_{ij}^{(\alpha)} = -v_{ji}^{(\bar{\alpha})}$. Therefore,

$$\begin{aligned} (v_{ij})_{eq} &= \frac{\sum (\omega_{ij}^{(\alpha)})_{eq} v_{ij}^{(\alpha)}}{(\omega_{ij})_{eq}} = \\ &= \frac{\sum_{\bar{\alpha}} (N_j / N_i)_{eq} \times (\omega_{ji}^{(\bar{\alpha})})_{eq} (-v_{ji}^{(\bar{\alpha})})}{(N_j / N_i)_{eq} \times (\omega_{ji})_{eq}} = \\ &= - \frac{\sum (\omega_{ji}^{(\bar{\alpha})})_{eq} v_{ji}^{(\bar{\alpha})}}{(\omega_{ji})_{eq}} = - (v_{ji})_{eq}. \end{aligned} \quad (E2)$$

It follows from this equation that the changes along the cycles are opposite:

$$\begin{aligned} (v_k)_{eq} &= \sum_{i \rightarrow j \in C_k} (v_{ij})_{eq} \\ &= \sum_{j \rightarrow i \in \bar{C}_k} - (v_{ji})_{eq} = -(\bar{v}_k)_{eq}. \end{aligned} \quad (E3)$$

Therefore, the contributions $(v_k)_{eq} [\Phi_k]_{eq}$ and $(\bar{v}_k)_{eq} [\bar{\Phi}_k]_{eq}$ from the Φ -graphs containing the counter cycles are mutually cancelled and the Eq. (46) is reduced to the equality $U_{eq} = 0$.

Appendix F

Let us show that the least possible magnitude of the exponent d in asymptotic dependence $U \propto PE^d$ in absence of degeneration and Auger processes is equal to $s - M + 1$. Here M is the number of the different states of a defect. $s = 2$ for bipolar and $s = 1$ for single polar injection. Indeed, the tree of maximal weight T covering the M -vertex digraph G will have an asymptotical weight $[T] \propto PE^t$, for which the exponent t may reach the maximal possible value $M - 1$, i.e. be equal to the number of the arcs of the M -vertex tree, if the weight of each arc will be proportional to PE^1 . This is the largest possible degree for the denominator in Eq.(50). At the same time, the smallest possible degree for the numerator coincides with the value of the above-mentioned parameter s .

Really, the cycle $\tilde{C}_k^\mu$ with non-zero $\tilde{v}_k^\mu$, should, of course, contain at least two transitions. One of them should be the electron capture from the conduction band and the another

one should be the hole capture from the valence band. Therefore weight of the cycle containing the product of probabilities of the two transitions will contain a factor PE^s . Weights of remaining arcs of the cycle will be proportional to PE^0 and PE^1 . Therefore, exponent for the cycle weight cannot be smaller, i.e. $\min \deg[\tilde{C}_k^\mu] = s$. The smallest degree for the weight $[\Psi_k]$ is equal to zero. It takes place when weights of all arcs forming the set of forests Ψ_k are proportional to PE^0 : $\min \deg[\Psi_k] = 0$. Then, according to Eq.(32), $\min \deg U = \min \deg[\tilde{C}_k^\mu] + \min \deg[\Psi_k] - \max \deg[T] = s + 0 - (M - 1)$. This is what has been stated above.

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