

## Thermodynamic basis of the concept of recombination resistance

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The concept of “recombination resistance” introduced by Shockley and Read [Phys. Rev. **87**, 835 (1952)] is discussed within the framework of the thermodynamics of irreversible processes ruled by the principle of the minimum rate of entropy production (MREP). It is shown that the affinities of recombination processes represent “voltages” in a thermodynamic Ohm-like law where the net rates of recombinations represent the “currents” and the Onsager coefficients of the phenomenological laws represent the inverse of the “resistances.” The quantities thus found allow for the definition of “dissipated power” which is to be related to the rate of entropy production of the recombination processes dealt with. The goal of this paper is thus to give a thermodynamical ground to the recombination resistance concept. But, also stressed is the potentiality of the MREP variational method. To this purpose, the simple case of the ideal (Shockley) diode, where diffusion forces are active as well, is considered.

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### I. INTRODUCTION

Crystal defects are physical entities of primary importance in solid state physics. Owing to the breaking of translational symmetry, they originate localized levels capable of trapping electrons or holes. On this ground, the physical properties of materials such as semiconductors can be modified by suitable doping determining the sign of majority carriers. Impurity or intrinsic defects may originate localized levels allowing recombinations of electron-hole pairs injected into bands by some excitation mechanism, thus affecting the lifetime of free carriers. The content of intrinsic defects at (lattice) equilibrium is ruled by general laws.<sup>1</sup> But in reality it strongly depends on the history of the sample dealt with. Depending on the nature of the defects, three basic schemes are to be considered. They are the Shon-Klasens (SK) scheme, in which a conduction band electron recombines with a hole kept in a localized level, the opposite Lamb-Klick (LK) scheme, in which a valence band hole recombines with a localized electron, and the Prener-Williams scheme, in which both electron and hole are localized within a two level center.<sup>2</sup>

At equilibrium, the occupation of electron (hole) levels is ruled by the Fermi-Dirac distribution  $f_n(E)[f_p(E)=1-f_n(E)]$ , that is,  $f_n(E)=1/\{1+\exp[(E-E_F)/kT]\}$  where  $E$  and  $E_F$  stand for the actual and the Fermi levels. The equilibrium densities of conduction band electrons and valence band holes are<sup>3</sup>  $\bar{n}=N_n\exp[(E_F-E_C)/kT]$  and  $\bar{p}=N_p\exp[(E_V-E_F)/kT]$ , respectively, where  $E_C$  and  $E_V$  are the energy levels of the bottom of the conduction band and of the top of the valence band, respectively,  $N_n=2(2\pi m_e kT/h^2)^{3/2}$  and  $N_p=2(2\pi m_p kT/h^2)^{3/2}$ ,  $m_e$  and  $m_p$  the electron and hole effective masses, respectively. It is to be pointed out that distinction between electron and hole traps is considered for convenience since only the capture cross section determines the trapping properties. Often, in the physics of semiconductors a hole trap is presented as a deep electron level, while a hole trapping level is presented as an acceptor level. In the physics of ionic crystals it is usual to define the trapping proper-

ties by means of the defect-charge states. Thus, negative charge defects are traps for holes (positive carriers). On the contrary, positive-charge defects are traps for electrons (negative carriers). But there are cases where these rules do not hold (for example, the  $U^-$  centers).<sup>4</sup> Also the distinction of carrier capture for trapping or recombination may be considered as conventional, since in both cases we are dealing with changes in level occupancies. Thus, for a general discussion about capture processes it is convenient to follow the model of trap classifications used by Simmons and Taylor (ST):<sup>5</sup> “When a trap is empty it is ready to receive an electron, and thus it is operating as an electron trap. When the trap contains an electron, it is ready to receive a hole, and hence is a hole trap. (We are assuming that the traps are monovalent.) It is convenient to assume that the traps existing below the equilibrium Fermi level are neutral when filled with an electron and that the traps positioned above the equilibrium Fermi level are neutral when empty. (...) Thus a trap positioned above the equilibrium Fermi level is neutral when acting as an electron trap and negatively charged when acting as a hole trap. On the other hand, a trap positioned below the equilibrium Fermi levels is neutral when acting as a hole trap and positively charged when acting as an electron trap.”

Departure from equilibrium can be obtained by different excitation sources. In this paper, we are considering ionizing photons causing band-to-band transitions. As the excitation source is turned on, carriers injected into the conduction and valence bands are drawn by the several processes occurring in the material, including trapping in metastable levels. The latter process allows crystals to attain excited states which can be held after the excitation source is turned off. In this case, the fundamental state can be reached by thermally stimulated processes.<sup>6</sup> Under steady excitation, the population of electron or hole levels attain a steady distribution after a time which, in some cases, may be very long.<sup>7</sup> The statistic of occupancy of the traps may be obtained from two different points of view. The first of these, which was used by Shockley and Read (SR),<sup>8</sup> considers the rate equations for the conduction and valence bands. The second, which was used by ST,<sup>5</sup> considers the rate equations for a particular

trapping center. In the nondegenerate case, both these approaches lead to an occupation  $f(E)$  of trap levels with energy  $E$  and density  $N_t(E)$  which is given by

$$f(E) = \frac{c_n n + c_p N_p \exp[(E_V - E)/kT]}{c_n \{n + N_n \exp[(E - E_C)/kT]\} + c_p \{p + N_p \exp[(E_V - E)/kT]\}}, \quad (1)$$

where  $c_n$  and  $c_p$  stand for the electron and hole capture probabilities, respectively. The basic assumption of the two approaches is that, at the steady state, the population of electron or hole levels can be described by means of a Fermi-Dirac-like function with suitable quasi-Fermi levels (QFL). For free carriers it was found that

$$\frac{np}{n_p} = \exp[(F_n - F_p)/kT], \quad (2)$$

where  $F_n$  and  $F_p$  stand for QFLs of free electrons and holes, respectively.

QFLs play a role in the rate of recombination processes. A suggestive idea introduced by SR considers the recombination rate at the steady state as a current passing through a resistance, called a “recombination resistance” (RR), depending on the kinetic parameters of the process dealt with. In the simplest cases, recombinations follow from two capture processes, that is, hole and electron capture, so that two resistances are to be considered, that is, near equilibrium

$$R_n = kT/\bar{n}p_0 c_n \quad (3)$$

for electron capture and

$$R_p = kT/\bar{p}n_0 c_p \quad (4)$$

for hole capture,  $\bar{n}_t = f_t N_t$  and  $\bar{p}_t = (1 - f_t) N_t$  standing for the equilibrium densities of trapped electrons and holes, respectively, and  $f_t$  for the level occupancy as given by the Fermi-Dirac function. By presenting QFLs as “voltages,” SR proved that in the near-equilibrium approximation the above resistance definitions allow for the equation

$$\mathcal{U}(R_n + R_p) = F_n - F_p, \quad (5)$$

which has the formal structure of Ohm’s law. SR also derived an equation for the lifetime of free carriers, that is,  $\tau = \bar{n}\bar{p}R/kT(\bar{n} + \bar{p})$  where  $R = R_n + R_p$ . About this point they concluded that “the effect of a number of different sorts of traps may be considered on the same basis. For each variety, the recombination is represented by a pair of resistances in series and these series pairs are combined in parallel for the entire system.”

At the level of the SR treatment we cannot immediately give a thermodynamic meaning to the product  $Rv^2$  which, in the theory of electricity, corresponds to the dissipated electrical power. In all probability, for this reason the concept of RR has remained an unexplored minor outcome of SR statistics although sometimes it is recalled in papers devoted to studies on the kinetics of electronic processes in semiconductor based devices.<sup>9</sup> The points are if, under certain circumstances, the rate of all the direct (band-to-band) and in-

direct (by localized levels) recombinations of conduction band electrons and valence band holes can depend, according to an Ohm-like law, on a thermodynamic force related to free carrier densities and what is the meaning of this. To examine these points, we investigate the recombination processes at the steady state from the general point of view of the thermodynamics of nonequilibrium. To this end, we remain in the range of linear irreversible processes, where it is possible to apply successfully the principle of minimum rate of entropy production (MREP). This approach resembles the one used (for a different scope) by V. Maxia.<sup>10</sup> The goal of this paper is to give a thermodynamic basis to the concept of RR. But, what is more, thermodynamics is universal so that chemical, solid state, and electrical processes can be handled together in a MREP variational procedure. In this connection it is shown that affinities are more suitable to represent “voltages” than QFLs. Actually, we are able to define the “resistances” of chemical reactions. What is better, it is shown that the analog of “dissipated power” is closely related to the rate of entropy production of the processes dealt with.

The paper is structured as follows. In Sec. II, basic concepts of nonequilibrium thermodynamics as well as the MREP principle are recalled. A suitable variational calculus based on the MREP principle is presented. All considerations are made for chemical reactions. In Sec. III, the results thus obtained are applied to typical recombination processes in semiconductors. In Sec. IV applications and limitations of the thermodynamic treatment are discussed. In particular, an equation for the affinity function is derived to account for the diffusion and recombination processes in an ideal (Shockley) diode. An extension to include photo-excitations in the diode is considered as well.

## II. THERMODYNAMICS OF THE NEAR-EQUILIBRIUM STEADY STATE

### A. Theory

Nonequilibrium thermodynamics lacks a constructive criterion such as the one given by maximum entropy for the equilibrium state. The latter provides a starting point for the application of statistical mechanics and thermodynamics. However, nonequilibrium thermodynamics shows that states having minimum entropy production compatible with the system constraints are stationary states.<sup>11</sup> In reality, this property characterizes the case of linear flux laws with constant phenomenological coefficients. Nevertheless, MREP allows for many nonequilibrium physical processes to be considered within a general framework.<sup>11</sup> Given the importance of this matter, it is convenient to recall some essential aspects of the

nonequilibrium theory, leaving details to the dedicated treatises.<sup>12</sup>

The basic equation of nonequilibrium thermodynamics is derived from the one by Gibbs. In general, the entropy change of a system can be written as

$$dS = d_e S + d_i S, \quad (6)$$

where  $d_e S$  is due to interaction with the system surroundings (actually, we are dealing with a closed system) and  $d_i S$  is the entropy production due to internal change of the system. In the case that internal changes are due only to chemical reactions, the entropy production term can be written as<sup>11</sup>

$$d_i S = -\frac{1}{T} \sum_{k=1}^c \mu_k dn_k, \quad (7)$$

where  $\mu_k$  is the chemical potential of the  $k$  component of a mixture containing  $c$  chemical species and  $dn_k$  is the corresponding molar change. For the ideal system  $\mu_k = \zeta_k + RT \ln N_k$  where  $\zeta_k$  is a quantity independent of actual composition and  $N_k$  is the molar fraction of the  $k$  component. If the system holds  $r$  chemical reactions, the molar change of the  $k$  component can be written as  $dn_k = \sum_{l=1}^r \nu_{kl} d\xi_l$  where  $\nu_{kl}$  is the stoichiometric coefficient of the  $k$  component in the  $l$  reaction which shows a “displacement”  $d\xi_l$ . Thus, the entropy production can also be written as

$$d_i S = -\frac{1}{T} \sum_{kl} \mu_k \nu_{kl} d\xi_l = \frac{1}{T} \sum_l \Gamma_l d\xi_l, \quad (8)$$

where  $\Gamma_l = -\sum_k \mu_k \nu_{kl} = -\sum_k \nu_{kl} \zeta_k - RT \sum_k \ln N_k^{\nu_{kl}}$  is the chemical affinity of the  $l$  reaction. At equilibrium the affinities vanish, so that  $\sum_k \nu_{kl} \zeta_k = -RT \sum_k \ln \bar{N}_k^{\nu_{kl}}$ . Thus, affinities can also be written as

$$\Gamma_l = -RT \ln \Pi_k (n_k / \bar{n}_k)^{\nu_{kl}}. \quad (9)$$

If at any instant the entropy changes as a function of chemical composition as well as other quantities characterizing the system, it is possible to write an equation for the rate of entropy production, that is,  $dS/dt = d_e S/dt + d_i S/dt$ , where

$$\frac{d_i S}{dt} = \frac{1}{T} \sum_l \Gamma_l v_l, \quad (10)$$

$v_l = d\xi_l/dt$  standing for the flux or velocity of the  $l$  reaction. It is assumed that near equilibrium fluxes are linear with respect to the affinities, that is,  $v_l = \sum_m L_{lm} \Gamma_m$  where  $L_{lm}$  are called the phenomenological coefficients.<sup>11</sup> As shown by Onsager,<sup>13</sup> based on the time reversal invariance of (microscopic) mechanical laws, the phenomenological coefficients form a symmetric matrix, that is  $L_{lm} = L_{ml}$ . It is to be pointed out that the criterion for sign assignments to stoichiometric coefficients is quite arbitrary. However, whatever the choice, if no external forces cause internal change,  $d_i S/dt \geq 0$  holds.

### B. Variational calculus

The separation of entropy contributions given in Eq. (6) may cause some problems of interpretation when the inter-

action with photons is considered. Classically speaking, the interaction with the electromagnetic (e.m.) field changes the density of internal energy with a rate given by the product  $\vec{E} \cdot \vec{j}$  where  $\vec{E}$  stands for the strength of electric field and  $\vec{j}$  for the vector of current density. Thus, a field releasing its energy to (emitted from) the system increases (decreases) the internal energy and thus the entropy. If configurational or chemical changes of the system are involved, the picture is slightly more complex. Actually, the e.m. field, which causes departure of the chemical reactions from equilibrium, reduces the entropy. A sequence of reactions brings the system to equilibrium, thus producing positive entropy. At the end of the process, the net change of chemical entropy is null. But reactions may produce heat and photons which alter the internal energy and thus the system entropy. Thus chemical reactions behave like a machine converting the absorbed photons to heat (and photons). About the entropy balance, further considerations will be advanced in Sec. IV. Now it appears convenient to write the rate of internal entropy production  $d_i S/dt$  as the sum of two contributions, that is

$$\frac{d_i S}{dt} = \sigma_{\text{ext}} + \sigma_{\text{int}}, \quad (11)$$

where  $\sigma_{\text{ext}}$  means the change of internal entropy due to external force and  $\sigma_{\text{int}}$  that due to the internal forces, that is, those bringing the system to equilibrium. The definitions of these two terms are to be searched for by means of the composition changes induced by absorbed photons, that is

$$dn_k = c_k \Phi dt + \sum_{l=1}^r \nu_{kl} d\xi_l, \quad (12)$$

where  $\Phi$  stands for the flux of the whole absorbed photons (in suitable units) and  $c_k$  for the fraction of photon flux inducing molar change of the  $k$  component. It follows from Eqs. (8) and (12) that

$$\frac{d_i S}{dt} = -\frac{1}{T} \Phi \Gamma_\Phi + \frac{1}{T} \sum_l \Gamma_l v_l, \quad (13)$$

where  $\Gamma_\Phi = -\sum_k (-c_k) \mu_k$  (we prefer this form to evidence that the entropy production of carrier photo-generation is negative) in the following will be referred to as external affinity or “force.”<sup>11</sup> We define

$$\sigma_{\text{ext}} = -\frac{1}{T} \Phi \Gamma_\Phi, \quad \sigma_{\text{int}} = \frac{1}{T} \sum_l \Gamma_l v_l. \quad (14)$$

Equation (13) can be generalized to include more independent sets of chemical reactions by adding further index labeling reaction sets, that is

$$\sigma_{\text{int}} = \frac{1}{T} \sum_{\gamma l} \Gamma_{\gamma l} v_{\gamma l}. \quad (15)$$

Variational procedures allowing for the MREP must account for the constraints that keep the system from equilibrium. These can be formalized by means of relations among affinities which are to be inserted in a Lagrange minimization procedure, where the affinities are the functional vari-

ables. We will see in Sec. III that the constraints have the form (see Appendix A)

$$\Gamma_{\Phi} - \sum_j \Gamma_{\gamma j} = 0, \quad \gamma = 1, \dots, r. \quad (16)$$

It is to be remarked that minimization concerns only  $\sigma_{\text{int}}$ , that is, only the internal processes bringing the system to equilibrium. However, to get a complete definition of the steady state, it is convenient to apply the minimization procedure to the function

$$\Omega = 2\sigma_{\text{ext}} + \sigma_{\text{int}} + \frac{1}{T} \sum_{\gamma} \lambda_{\gamma} \left( \Gamma_{\Phi} - \sum_j \Gamma_{\gamma j} \right), \quad (17)$$

by including  $\Gamma_{\Phi}$  among the functional variables. Factor 2 takes into account that  $\sigma_{\text{int}}$  is a quadratic form on the affinities (this procedure is substantially different from that used in Ref. 10). It is easy to check the consistence of this variational procedure. Indeed, as a result, it is obtained that  $\Phi = \sum_{\gamma} \lambda_{\gamma} / 2$  and  $v_{\gamma} \equiv v_{\gamma l} = \lambda_{\gamma} / 2$ ,  $l = 1, \dots, r$ , that is,  $\Phi = \sum_{\gamma} v_{\gamma}$ . Thus, at the steady state the fluxes within a reaction set are the same for all reactions and the whole flux of reaction sets is equal to the flux of absorbed photons.

In this paper we are concerned with reactions allowing for a diagonal Onsager's matrix. The diagonal Onsager's matrix is peculiar to reactions that do not show interference effects so that<sup>11</sup>

$$v_{\gamma l} = L_{\gamma l} \Gamma_{\gamma l}, \quad l = 1, \dots, c. \quad (18)$$

Thus, by taking into account Eq. (16) it follows:

$$v_{\gamma} = \frac{\Gamma_{\Phi}}{\sum_j 1/L_{\gamma j}}. \quad (19)$$

Note that, at the steady state, flux is independent of the reaction index but depends only on the reaction-set index. The reaction affinity is related to the external force by the equation

$$\Gamma_{\gamma l} = \Gamma_{\Phi} \frac{1/L_{\gamma l}}{\sum_j 1/L_{\gamma j}}. \quad (20)$$

Now, by defining the RRs as

$$R_{\gamma l} = 1/L_{\gamma l}, \quad (21)$$

we are able to describe a set of chemical reactions, activated by the photon flux with external force  $\Gamma_{\Phi}$ , as a current  $v_{\gamma}$  passing through a series of resistances  $R_{\gamma j}$  to which is applied a voltage  $\Gamma_{\Phi}$ . Thus, the drop in voltage on the resistance  $R_{\gamma j}$ , that is,  $\Gamma_{\gamma j} = R_{\gamma j} v_{\gamma}$ , can be calculated by means of Eq. (20) which gives the voltage partition, that is

$$\Gamma_{\gamma l} = \frac{R_{\gamma l}}{\sum_j R_{\gamma j}} \Gamma_{\Phi}. \quad (22)$$

The series resistances of a reaction channel have an equivalent resistance  $R_{\gamma \text{EQ}} = 1/L_{\gamma \text{EQ}} = \sum_l 1/L_{\gamma l} = \sum_l R_{\gamma l}$ . The rate of all chemical reactions is obtained from

$$v = \sum_{\gamma} v_{\gamma} = \left( \sum_{\gamma} L_{\gamma \text{EQ}} \right) \Gamma_{\Phi} = L_{\text{EQ}} \Gamma_{\Phi}, \quad (23)$$

where  $L_{\text{EQ}}$  can be associated to the equivalent resistance of the parallel reaction resistances  $R_{\gamma \text{EQ}}$ , that is,  $1/R_{\text{EQ}} = L_{\text{EQ}} = \sum_{\gamma} L_{\gamma \text{EQ}} = \sum_{\gamma} 1/R_{\gamma \text{EQ}}$ . Finally, for full correspondence to Ohm's law we must give a meaning to the Joule equation for the dissipated power, that is

$$W = \sum_{\gamma} v_{\gamma} \Gamma_{\Phi} = \sum_{\gamma} v_{\gamma} \sum_j \Gamma_{\gamma j} = T \sigma_{\text{int}}, \quad (24)$$

which corresponds to the rate of entropy production multiplied by temperature. This has an evident meaning: As the electrical work dissipates the electric potential energy by producing heat, the chemical reactions dissipate the stored chemical energy by producing entropy (in general there is production of heat and photons).

We remark that Eq. (23) is local. In the context of MREP this is a consequence of having minimized entropy production with respect to the affinities which are defined by means of the actual (local) concentrations. Thus we can use Eq. (23) even when spatially dependent affinities are dealt with. In this case diffusion forces are to be accounted for. This point will be dealt with in detail in Sec. IV.

### III. APPLICATION TO ELECTRON-HOLE RECOMBINATIONS

Until now, for simplicity, we have considered cases where internal changes are to be ascribed to chemical reactions. To deal with electron-hole recombinations we should consider more suitable units, that is, densities ( $\text{cm}^{-3}$ ) rather than molar concentrations. To this end, we must divide the rate of entropy production by molar volume  $V_M$  ( $\text{cm}^3$ ), so that

$$\frac{v\Gamma}{V_M} = - \frac{d(N_0 \xi / V_M)}{dt} kT \ln \Pi_k (n_k / \bar{n}_k)^{v_k},$$

where  $N_0$  stands for the Avogadro number, the other symbols having the usual meanings. Now,  $dN_0 \xi / V_M / dt$  is the reaction flux with the desired units, that is,  $\text{cm}^{-3} \text{s}^{-1}$ . In the following, as a consequence of this unit choice, the affinities will be calculated as

$$\Gamma = -kT \ln \Pi_k (n_k / \bar{n}_k)^{v_k}.$$

#### A. SK and LK cases

Near equilibrium (but also in most practical cases) the rate equations can be written in the approximation of nondegenerate statistics, that is, emission rates of trapped carriers released into bands are independent of the occupation of band levels. In this approximation, rate equations assume a very simple form.<sup>8,10</sup> For simplicity's sake, it is convenient to begin by considering the cases of SK and LK. Formally, they can be dealt with as a single case. Indeed, they differ only in what kind of carrier is trapped and what is recombined, that is, if an electron is recombined with a trapped hole or, conversely, if a hole is recombined with a trapped electron. As stated in Sec. I, this difference has no formal relevance since

it is due only to actual level position with respect to the equilibrium Fermi level

Let  $N_t$  mean the density of defects,  $p_t$  the actual density of trapped holes (traps empty of electrons),  $n_t$  the density of traps empty of holes (filled with electrons), so that  $N_t = p_t + n_t$ . Owing to interactions with ionizing radiations, electrons and holes are injected into conduction and valence bands, respectively, with a rate  $\Phi$ . Carriers are captured with probability  $c_e$ , for conduction band electrons, and  $c_p$ , for valence band holes, respectively. Thermal releasing of electrons into conduction bands and of holes into valence bands occurs with probabilities  $s_e$  and  $s_p$  (included is the interaction with blackbody radiation), respectively. Thus, the net rate of electron capture is<sup>8</sup>

$$v_n = c_e n p_t - s_e n_t \quad (25)$$

and that of hole capture is

$$v_p = s_p p_t - c_p p n_t. \quad (26)$$

At equilibrium  $v_n = v_p = 0$ . Thus,

$$\frac{\overline{n p_t}}{\overline{n_t}} = \frac{s_e}{c_e}, \quad (27)$$

$$\frac{\overline{p n_t}}{\overline{p_t}} = \frac{s_p}{c_p}. \quad (28)$$

To define affinities, we need to fix a positive direction for processes as a sign reference for stoichiometric coefficients. Let us take as the positive direction that of the arrow pointing from the valence to the conduction band. Thus, the terms representing processes which bring electrons toward the valence band, as well as holes toward the conduction band, are associated with the stoichiometric coefficient equal to  $-1$ . The opposite sign is associated with the terms describing processes in the opposite direction. On this ground, the electron affinity is

$$\Gamma_n = -kT \ln \left[ \left( \frac{n}{\overline{n}} \right)^{\nu_a} \left( \frac{n_t}{\overline{n_t}} \right)^{\nu_b} \left( \frac{p_t}{\overline{p_t}} \right)^{\nu_c} \right] \quad (29)$$

with  $\nu_a = \nu_c = -1$ , since  $n$  and  $p_t$  appear in a term of negative direction, and  $\nu_b = +1$ , since  $n_t$  appears in a term of positive direction. Thus, we can write

$$\Gamma_n = -kT \ln \left( \frac{n_t \overline{n p_t}}{n p_t \overline{n_t}} \right). \quad (30)$$

The hole affinity can be obtained in an analogous way, that is,

$$\Gamma_p = -kT \ln \left( \frac{p_t \overline{p n_t}}{p n_t \overline{p_t}} \right). \quad (31)$$

The external affinity is

$$\Gamma_\Phi = -kT \ln \left[ \left( \frac{n}{\overline{n}} \right)^{-c_a} \left( \frac{p}{\overline{p}} \right)^{-c_b} \right]$$

with  $c_a = c_b = +1$  since the reaction is on the positive direction. Thus

$$\Gamma_\Phi = kT \ln \left( \frac{n p}{\overline{n p}} \right), \quad (32)$$

so that the loop constraint (16) is satisfied, that is,  $\Gamma_\Phi - (\Gamma_1 + \Gamma_2) = 0$ . For steady states near equilibrium we can write, approximately,

$$v_n = c_e \overline{n p_t} \left( 1 - \frac{n_t \overline{n p_t}}{n p_t \overline{n_t}} \right), \quad (33)$$

$$v_p = c_p \overline{p n_t} \left( 1 - \frac{p \overline{p n_t}}{p n_t \overline{p_t}} \right). \quad (34)$$

In the same approximation, the latter equations can be re-written as

$$v_n = \frac{c_e \overline{n p_t}}{kT} \Gamma_n = L_n \Gamma_n, \quad (35)$$

$$v_p = \frac{c_p \overline{p n_t}}{kT} \Gamma_p = L_p \Gamma_p, \quad (36)$$

where

$$L_n = \frac{c_e \overline{n p_t}}{kT}, \quad L_p = \frac{c_p \overline{p n_t}}{kT} \quad (37)$$

are the Onsager's coefficients. Finally, by definitions, the RRs are

$$R_n = \frac{1}{L_n} = \frac{kT}{c_e \overline{n p_t}}, \quad R_p = \frac{1}{L_p} = \frac{kT}{c_p \overline{p n_t}},$$

which agree with that found by SR [see Eqs. (3) and (4)]. Note that the steady current is

$$v = v_n = v_p = \frac{\Gamma_\Phi}{R_n + R_p},$$

so that

$$\mathcal{U}(R_n + R_p) = \Gamma_\Phi.$$

By taking into account the definitions of QFLs for free carriers [see Eq. (2)], it follows:

$$\Gamma_\Phi = kT \ln n p / \overline{n p} = F_n - F_p,$$

so that

$$\mathcal{U}(R_n + R_p) = F_n - F_p,$$

which is exactly the result found by SR [Eq. (5)].

Note also that, according to SR [by integrating Eq. (2.9) of Ref. 8 over the whole states of conduction band]

$$\frac{\overline{n p_t}}{\overline{n_t}} = \frac{s_e}{c_e} = N_n \exp[(E_t - E_C)/kT], \quad (38)$$

where  $E_t$  stands for the energy of the trapping level. Now, by taking into account that

$$\frac{n_t}{p_t} = \frac{f_t}{1 - f_t} = \exp[-(E_t - F_t)/kT] \quad (39)$$

$f_t$  being the occupancy of electron traps with QFL  $F_t$ , it follows from Eqs. (30) and (31) that

$$\Gamma_n = F_n - F_t. \quad (40)$$

Analogously, for the affinity of the trapped hole it can be shown that

$$\Gamma_p = F_t - F_p. \quad (41)$$

Equations (40) and (41) allow for a full correspondence to the SR results.

### B. PW case

In their paper SR considered only recombinations in single level centers, as in SK or LK processes. Now, it is advisable to consider also the case of two-level recombination centers as in the PW processes. With respect to the SK (or LK) two-step processes, in the PW case we must consider a further step, that is, the recombinations of electrons trapped in levels labeled, say, 1 with holes trapped in levels labeled, say, 2. The corresponding recombination rate is

$$v_\omega = \pi n_{1t} p_{2t} - s_\omega p_{1t} n_{2t}, \quad (42)$$

where  $\pi$  stands for the recombination probability,  $n_{1t}$  and  $p_{1t}$  for the densities of electrons and holes trapped at the level labeled 1, respectively,  $n_{2t}$  and  $p_{2t}$  for the densities of electrons and holes trapped at the level labeled 2, respectively, and  $s_\omega$  for the probability of pair production by thermal excitation. At equilibrium

$$\frac{\bar{n}_{1t} \bar{p}_{2t}}{\bar{p}_{1t} \bar{n}_{2t}} = \frac{s_\omega}{\pi}, \quad (43)$$

so that

$$v_\omega = \pi \bar{n}_{1t} \bar{p}_{2t} \left( 1 - \frac{p_{1t} n_{2t} \bar{n}_{1t} \bar{p}_{2t}}{n_{1t} p_{2t} \bar{p}_{1t} \bar{n}_{2t}} \right). \quad (44)$$

It is easy to verify that the affinity is

$$\Gamma_\omega = -kT \ln \frac{p_{1t} n_{2t} \bar{n}_{1t} \bar{p}_{2t}}{n_{1t} p_{2t} \bar{p}_{1t} \bar{n}_{2t}}. \quad (45)$$

Thus by using the definitions of electron and hole affinities (obtained in the previous section) suitably modified to account for the index levels, it is easy to prove that  $\Gamma_\omega = \Gamma_{n1} + \Gamma_\omega + \Gamma_{p2}$ . Now, the flux of the recombination process is

$$v_\omega = L_\omega \Gamma_\omega = L_\omega [\Gamma_\omega - (\Gamma_{n1} + \Gamma_{p2})], \quad (46)$$

where

$$L_\omega = \pi \bar{n}_{1t} \bar{p}_{2t} / kT \quad (47)$$

to which is associated the RR

$$R_\omega = 1/L_\omega = kT / \pi \bar{n}_{1t} \bar{p}_{2t}. \quad (48)$$

The current through the recombination channel is

$$v = \frac{\Gamma_\omega}{R_{n1} + R_{p2} + R_\omega}. \quad (49)$$

Note that the affinity  $\Gamma_\omega$  is related to QFLs by the equation  $\Gamma_\omega = F_{t1} - F_{t2}$ .

### C. Case of band-to-band recombination

As a final example, let us calculate the RR associated with band-to-band recombinations which now appears as an easy task. Briefly, the net rate of recombinations is  $v_G = \pi_G n p - s_G$  where  $\pi_G$  stands for the probability of electron-hole pair recombination and  $s_G$  for the thermal emission of electrons from the valence to conduction band. At equilibrium  $\bar{n} \bar{p} = s_G / \pi_G$ . Thus  $v_G = \pi_G \bar{n} \bar{p} (1 - \bar{n} \bar{p} / np) = L_G \Gamma_G$  where  $\Gamma_G = \Gamma_\Phi$  and  $L_G = \pi_G \bar{n} \bar{p} / kT$ . The associated RR is  $R_G = 1/L_G = kT / \pi_G \bar{n} \bar{p}$ , so that the current can be written as  $v_G = \Gamma_\Phi / R_G$ .

## IV. DISCUSSION

In the previous section we considered three main mechanisms of recombinations in localized levels. We point out that the algorithm implemented to obtain the Onsager coefficients and, thus, the RRs is general. Let us briefly consider recombinations involving formation of excitons. The process to be considered is *electrons+holes*  $\rightleftharpoons$  *excitons* as well as that of exciton annihilation-generation. These define an indirect channel of free electron-hole recombinations whose affinity is still  $\Gamma = kT \ln(np/\bar{n}\bar{p})$ . The probability factors involved thus determine the corresponding RR which is to be considered in parallel to the others.

Until now we have assumed that electrons, holes, and phonons have the same temperatures. If this is not the case, the Ohm representation may fail. Thus we have to search for an additional condition that saves this representation when differences of temperatures are to be considered.<sup>14</sup> Before dealing with this point in general, we consider the case of band-to-band recombinations. Let  $\delta\pi_G$  and  $\delta s_G$  mean the variation of kinetic parameters with respect to the equilibrium values  $\bar{\pi}_G$  and  $\bar{s}_G$  at the phonon temperature  $T_{ph}$ . The net recombination rate in the linear range is

$$\begin{aligned} v_G &= \bar{\pi}_G n p - \bar{s}_G + \bar{n} \bar{p} \delta\pi_G - \delta s_G \\ &\approx L_G \left[ \Gamma_G + kT_{ph} \delta \ln \left( \frac{\pi_G \bar{s}_G}{\bar{\pi}_G \bar{s}_G} \right) \right] = L_G \tilde{\Gamma}_G, \end{aligned}$$

where now  $\Gamma_G$  is the difference of QFLs at  $T_{ph}$  and  $\tilde{\Gamma}_G$  may be referred to as the generalized affinity which, by defining  $\bar{n}^* \bar{p}^* = s_G / \pi_G$ , becomes  $\tilde{\Gamma}_G = kT_{ph} \ln(np/\bar{n}^* \bar{p}^*)$ . With analogous considerations, the net recombination rate of a generic  $l$  process can be written as

$$v_l \approx L_l \left[ \Gamma_l - kT_{ph} \delta \ln \left( \prod_j \frac{\bar{a}_{lj}}{a_{lj}} \right)^{v_{lj}} \right], \quad (50)$$

where the  $a_l$  are the corresponding kinetic parameters,  $v_{lj}$  having the usual meanings. Owing to the additional term, the Ohm picture cannot represent recombinations unless in any closed (Markovian) chain the condition  $\sum_l \delta \ln(\prod_j \bar{a}_{lj}/a_{lj})^{v_{lj}} = 0$  holds. Note that if the local temperature changes with coordinates the local equilibrium reference state, affinities and Onsager coefficients change as well. In this case, the dependence of RRs on coordinates is to be investigated by the MREP method applied to the entropy production of the whole semiconductor volume. This investigation is out of the scope of this paper.

Recombination resistances may have a spatial dependence in nonhomogeneous semiconductors. Their investigation can be difficult when changes occur in the range of very small dimensions. Indeed, in the case of systems as small as 2–5 nm, even the definition of nonequilibrium temperature is difficult.<sup>15</sup> However, even at a more affordable nanoscale and mesoscopic range there remains the problem of taking into account the entropy barriers due to boundary of domains.<sup>16</sup> Moreover, complexities such as surface or interface effects, tunnel processes, hot carriers, etc., may make the use of RR picture impracticable. In reality, it calls for bulk semiconductor physics where lifetime of carriers plays a role in the transport properties. To better illustrate this point let us consider the simple case of the ideal (Shockley)  $p$ - $n$  diode.<sup>17</sup> In the linear range, the continuity equations of free carriers are<sup>18</sup>

$$\mathbf{D}_n \nabla^2 \mathbf{n} - \bar{n} \kappa_n \nabla^2 \mathbf{V} - \mathbf{v} = \mathbf{0}, \quad (51)$$

$$D_p \nabla^2 p + \bar{p} \kappa_p \nabla^2 V - \mathbf{v} = 0, \quad (52)$$

where  $V$  stands for the voltage in the diode,  $\kappa_n$  and  $\kappa_p$  for the mobilities of electrons and holes, respectively, and  $\mathbf{v}$  for the local net rate of recombinations. It was found that Eqs. (51) and (52) are consistent with the MREP principle.<sup>18</sup> The continuity equations can be written to include photoexcitation by substitution  $\mathbf{v} \rightarrow \mathbf{v} - \Phi$ . From the point of view of the MREP method, the variational calculus is to be applied to an entropy production function including diffusion forces and modified as Eq. (17). By using the Einstein relations, that is,  $eD_p/\kappa_p = eD_n/\kappa_n = kT$ , and by taking into account that in the linear range  $\nabla^2 \Gamma \approx (1/\bar{n})\nabla^2 n + (1/\bar{p})\nabla^2 p$ , we obtain from the combination of Eqs. (51) and (52)

$$\nabla^2 \Gamma - kT \frac{L}{D_p D_n} \left( \frac{D_p}{\bar{n}} + \frac{D_n}{\bar{p}} \right) \Gamma = 0. \quad (53)$$

Now, let us define the free carrier lifetimes as  $\tau_p = \bar{p}/kT L_{EQ}$  as  $\tau_n = \bar{n}/kT L_{EQ}$ , which allow for the definitions of diffusion length of electrons,  $l_n = \sqrt{D_n \tau_n}$ , and holes,  $l_p = \sqrt{D_p \tau_p}$ . By defining the characteristic length  $l$  of the affinity function as

$$\frac{1}{l^2} = kT \frac{L_{EQ}}{D_p D_n} \left( \frac{D_n}{\bar{n}} + \frac{D_p}{\bar{p}} \right) = \frac{1}{D_p \tau_p} + \frac{1}{D_n \tau_n} = \frac{1}{l_p^2} + \frac{1}{l_n^2} \quad (54)$$

Eq. (53) becomes  $\nabla^2 \Gamma - \Gamma/l^2 = 0$ . For simplicity's sake, in the following we refer to the Shockley's diode scheme.<sup>19</sup> Densities depend on the  $x$  coordinate only, the edge of the  $p$  region is at  $x=0$  and  $x_{Tp}$  and  $x_{Tn}$  mark the transition region in the  $p$  and  $n$  side, respectively. Thus, the affinity equation becomes

$$\frac{\partial^2 \Gamma}{\partial x^2} - \frac{\Gamma}{l^2} = 0. \quad (55)$$

As boundary condition for the solution of Eq. (55) we require only that far from the biased junction the affinity vanishes (owing to the equality between electron and hole QFLs: local equilibrium). Consequently, the affinity is

$$\Gamma(x) = \Gamma(x_{Tp}) \exp[(x - x_{Tp})/l], \quad x \leq x_{Tp},$$

$$\Gamma(x) = \Gamma(x_{Tn}) \exp(x_{Tn} - x/l), \quad x \geq x_{Tn}, \quad (56)$$

the length  $l$  being constant (but not necessarily equal) in the homogeneous regions. The electrical current in the semiconductor is due to recombinations of minority carriers beyond the transition region. The net rate of recombinations over the whole diode is

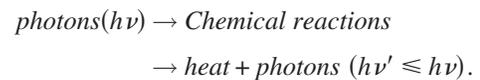
$$G = \int \mathbf{v} dx = A(L_{EQ})_n \int_{n \text{ side}} \Gamma dx + A(L_{EQ})_p \int_{p \text{ side}} \Gamma dx, \quad (57)$$

$A$  being the cross section area of the diode. In the case of semi-infinite homogeneous regions, the electrical current  $I = eG$  is thus  $I = eS((L_{EQ})_p \Gamma_1(x_{Tp}) + (L_{EQ})_n \Gamma_1(x_{Tn}))$ . Let us define  $r_{EQ} = R_{EQ}/e^2 S l$  as the electrical RR normalized with respect to the volume of the semiconductor whose thickness is as wide as the diffusion length. Thus

$$I = \frac{\Gamma(x_{Tp})}{e(r_{EQ})_p} + \frac{\Gamma(x_{Tn})}{e(r_{EQ})_n}. \quad (58)$$

Note that extension to the nonlinear range can be obtained from the substitution<sup>20</sup>  $\Gamma \rightarrow kT[\exp(\Gamma/kT) - 1]$ . Thus, in the language of RR, the saturation currents are  $I_{Sp} = kT/e(r_{EQ})_p$  and  $I_{Sn} = kT/e(r_{EQ})_n$  for holes and electrons, respectively.<sup>19</sup> In the case of photoexcited diode, we must add  $-\Phi(x)/l^2 L_{EQ}$  to the right side of Eq. (55) where the actual dependence of  $\Phi(x)$  on coordinates is determined by the condition of illumination (edge or uniform) as well as on cross sections of elementary photo-excitations.

At the steady state, the entropy of the system is time independent so that  $dS/dt = 0$ , that is,  $d_e S/dt = -d_i S/dt$ . From Eq. (13) and by taking into account of the results of variational calculus we see that  $d_i S/dt = 0$ . This result is expected since the chemical composition is time independent as well. Nevertheless, it is worth dwelling upon this point to complete the considerations in Sec. II. Actually, the entropy balance is based on the following scheme:



A flux of energy carried by photons, owing to internal reactions, is partly converted to heat and partly to photons (of lesser energy). The rate of heat production is thus  $dQ/dt = \Phi(h\nu - h\nu')$  which, divided by the system temperature, is to be considered as the indirect contribution to  $d_e S/dt$  due to the flux of ionizing photons. But the system is not isolated, so that the heat produced by reactions is thus released to surroundings. This causes at the steady state  $d_e S/dt = 0$  but a positive entropy is released to the surroundings thus contributing to the increase in the entropy of the universe.

The definitions of RR rely on the diagonal property of the Onsager's matrix associated with the recombination processes. Besides some nice cases, the generalization to nondiagonal processes does not appear to be possible. In Appendix B we try to diagonalize the thermodynamic problem of a two-reaction process that satisfies Eq. (21).

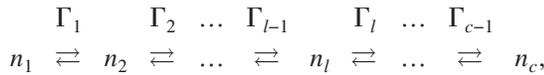
We again stress that the results found in this paper hold in the linear range of nonequilibrium thermodynamics. In this connection, it is understood that they are to be considered in the same spirit as one considers the linear approximation when small deviations from linearity can be disregarded.<sup>21</sup> The validity of MREP far from equilibrium is still debated.<sup>22</sup> Moreover, in general, relations among fluxes and forces are not linear. However, linearization of relations is possible provided the system dealt with is near the steady state considered as the “reference state.”<sup>23</sup> Unfortunately, the matrix of coefficients is not symmetric for long. Thus, at the moment, definitions of RRs (which conserve thermodynamic meanings) for processes far from equilibrium appear a difficult task.

## V. CONCLUSIONS

In this paper the electron-hole recombinations in an excited material near equilibrium has been investigated within the framework of the nonequilibrium thermodynamics ruled by the MREP principle. A formal Ohm-like law has been proved to hold for recombinations, thus giving a thermodynamic ground to the concept of recombination resistances, as defined by Shockley and Read. These are found to be related to the Onsager coefficients of the phenomenological laws. The entropy produced by recombinations is found to obey a Joule-like law where (multiplied by temperature) it plays the role of the “dissipated power.” This makes the correspondence between steady electron-hole recombinations and electrical processes complete, at least when linear flux laws hold. As an example, an application to the simple ideal (Shockley) diode is presented and an equation for the affinity function, which can be easily extended to include photoexcitations, is derived.

## APPENDIX A

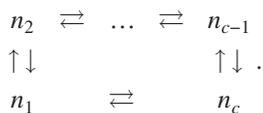
The reactions dealt with in this paper can be represented by means of a chain-process scheme, that is,



where the  $l$ th reactions depend only on the  $l$  and the  $l+1$  components. From Eq. (9) it follows that the whole affinity is ( $v_{l,l+1} = -v_{l+1,l} = 1$ )

$$\Gamma = \sum_{l=1}^{c-1} \Gamma_l = - \sum_{l=1}^{c-1} RT \ln \Pi_k \left( \frac{n_k}{\bar{n}_k} \right)^{v_{kl}} = RT \ln \left( \frac{n_1 n_c}{\bar{n}_1 \bar{n}_c} \right).$$

Now, let the above set of reactions form a closed loop. Thus, we have to further consider a reaction  $n_c \rightleftharpoons n_1$  with affinity  $\Gamma_c$ , that is,



In this case  $\sum_l \Gamma_l = 0$  so that

$$\Gamma_c = - \sum_{l=1}^{c-1} \Gamma_l = -\Gamma = \mu_1 - \mu_c.$$

If an external force  $\Gamma_F$  moves the system from equilibrium between components 1 and  $c$ , it is opposite to the  $\Gamma_c$  force that brings the system towards equilibrium, that is,  $\Gamma_F = -\Gamma_c$ . Thus,

$$\Gamma_F = \Gamma = \sum_{l \neq c} \Gamma_l$$

from which we obtain Eq. (16).

## APPENDIX B

Now let us consider a case where Eq. (16) holds but the symmetric Onsager’s matrix is not diagonal. Let us consider a two-component reaction set with fluxes

$$v_1 = L_{11}\Gamma_1 + L_{12}\Gamma_2, \quad v_2 = L_{21}\Gamma_1 + L_{22}\Gamma_2,$$

which can be rewritten as

$$v_1 = (L_{11} - L_{12})\Gamma_1 + L_{12}\Gamma_\Phi, \quad v_2 = L_{21}\Gamma_\Phi + (L_{22} - L_{21})\Gamma_2.$$

At the steady state  $v_1 = v_2$  so that

$$\Gamma_i = \frac{(L_{jj} - \eta)}{(L_{11} - \eta) + (L_{22} - \eta)} \Gamma_\Phi,$$

where  $j \neq i$  and  $\eta = L_{12} = L_{21}$ . Moreover we see that

$$v_i = \left[ \frac{(L_{11} - \eta)(L_{22} - \eta)}{(L_{11} - \eta) + (L_{22} - \eta)} + \eta \right] \Gamma_\Phi,$$

which does not have the formal structure of Ohm’s law. But, by defining the new fluxes

$$\tilde{v}_i = v_i - \eta \Gamma_\Phi = \frac{(L_{11} - \eta)(L_{22} - \eta)}{(L_{11} - \eta) + (L_{22} - \eta)} \Gamma_\Phi$$

and the new phenomenological coefficients

$$\tilde{L}_{ii} = L_{ii} - \eta$$

we are able to diagonalize the thermodynamic problem provided a new flux is considered, that is,

$$\tilde{v}_\Phi = \eta \Gamma_\Phi.$$

Consequently, the variational calculus is to be applied to the function

$$\Omega = -2 \frac{\Phi \Gamma_\Phi}{T} + \frac{\tilde{v}_1 \Gamma_1}{T} + \frac{\tilde{v}_2 \Gamma_2}{T} + \frac{\tilde{v}_\Phi \Gamma_\Phi}{T} + \frac{1}{T} \lambda [\Gamma_\Phi - (\Gamma_1 + \Gamma_2)].$$

Now, we can define the reaction resistances as  $R_i = 1/(L_{ii} - \eta)$  and  $R_\Phi = 1/\eta$ , where  $R_\Phi$  is to be considered in parallel with the other two resistances. Note that in the case  $L_{ii} = \eta$  it follows that  $v_1 = v_2 = \eta \Gamma_\Phi$ , and  $\tilde{v}_1 = \tilde{v}_2 = 0$  which is consistent with the infinite resistance.

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