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Irreversible Thermodynamics and Carrier Density Fluctuations in Semiconductors

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The formalism of irreversible thermodynamics is applied to the kinetics of carrier transitions in semiconductors. The thermodynamic forces, the generalized resistances and admittance functions are introduced. It is shown that the thermodynamic forces which establish the regression of a perturbed state to equilibrium are the differences of the quasi-Fermi levels that have to be assigned to each group of carriers; the generalized resistances are simply related to the transition rates. It is then possible to write the kinetic equations for the rate of change of the various carrier concentrations in a unified form so that the dissipation-fluctuation theorem of Callen and Greene can be applied. The spectral density matrix of the spontaneous carrier fluctuations is immediately found from the admittance matrix. The results can be expressed in a closed form which is valid for nondegenerate as well as for degenerate semiconductors. An electrical network analog is also outlined. The theory is applied explicitly to electronic noise in extrinsic and near-intrinsic crystals with and without recombination centers. Finally, the close connection with statistical results obtained before is discussed and the complete agreement between the Einstein relation and the extended "*g-r* theorem" for the variances is established.

INTRODUCTION

CARRIER concentration disturbances in semiconductors have been studied in great detail in recent years. Several contributions appeared on the decay of injected carriers to the equilibrium state. Often, a main object is to find the relaxation times of the regression process, which informs us about the nature of the energy levels involved. The theories which deal with these processes usually are based on a simple kinetic approach. Although the equilibrium behavior of the carrier densities can be deduced from thermodynamic arguments (e.g., from the minimum of the electronic free energy) no attempt has been made to describe generation-recombination processes in a nonequilibrium state with irreversible thermodynamics, as far as the author knows. This formalism will be developed here and it will be shown that it gives a thorough basis for concepts as quasi-Fermi levels, recombination resistances, etc., which were used before in a heuristic way. Also, the proper lifetimes for injected carrier densities can be found in a general fashion. The merit of the method, however, is not the computation of carrier relaxation times which can be obtained by direct statistical considerations in a much simpler way. On the contrary, the method is extremely useful for the calculation of the spontaneous fluctuations in the carrier densities, which occur under thermal equilibrium. It is in view of these fluctuations that we develop the theory here.

The connection between irreversible thermodynamics and fluctuation theory dates from the foundation of this branch of physics by Onsager[1] who proved the so-called reciprocity relations for macroscopic transport phenomena with the aid of the principle of microscopic reversibility of the fluctuation processes. These Onsager relations are still basic for many irreversible processes.[2] The theory of fluctuations, in turn, has greatly benefitted from the development of irreversible thermodynamics. Fundamental results were obtained by Onsager and Machlup[3] and by Tisza and Manning.[4] The latter authors showed that the Boltzmann-Einstein theorem, which relates the entropy and the steady-state distribution functions for the extensive parameters, has an analog for the nonsteady state in which a general relationship exists between the dissipation function and the conditional Markoff probability dealing with the change of the fluctuations in the course of the time. This theorem permits a calculation of the fluctuations in the time domain (correlation functions) from irreversible-thermodynamical concepts. We shall not employ this method here since, from an experimental point of view, the spectrum of the fluctuations is of more importance. Preferring therefore the frequency domain, we shall avail ourselves of a very important theorem, established by Callen and Greene[5] and others,[6,7] known as the fluctuation-dissipation theorem or generalized Nyquist formula. This theorem states that the spectral densities of the fluctuating extensive thermodynamic parameters are simply $4kT/\omega^2$ times the real part of admittance functions which relate forces and fluxes in a perturbed system. A well-known example is thermal noise in electrical networks where a mere calculation of the total admittance suffices to find the noise. To stress the importance of this theorem we will briefly review the customary methods employed in the analysis of stochastic processes.

1. General Remarks about the Method to Be Followed

Let x_i be the fluctuating quantities in which we are interested. In many cases these quantities satisfy

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[1] L. S. Onsager, Phys. Rev. **37**, 405 (1937); also Phys. Rev. **38**, 2265 (1937).

[2] A comprehensive account by S. R. de Groot is found in *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951).

[3] L. S. Onsager and S. Machlup, Phys. Rev. **91**, 1505 and 1512 (1953).

[4] L. Tisza and I. Manning, Phys. Rev. **105**, 1695 (1957).

[5] H. B. Callen and R. F. Greene, Phys. Rev. **86**, 702 (1952); R. F. Greene and H. B. Callen, Phys. Rev. **88**, 1387 (1952).

[6] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

[7] J. Weber, Phys. Rev. **101**, 1620 (1956).

Langevin equations

$$dx_i/dt=\sum_j A_{ij}x_j+\epsilon_i(t). \tag{1.1}$$

These equations are obtained by adding noise source terms $\epsilon_i(t)$ to the appropriate macroscopic kinetic equations, e.g., network equations when dealing with thermal electrical noise, or linearized carrier "reaction equations" containing all recombination and generation terms in the case under discussion here (compare van Vliet and Blok[8]). Equations (1.1) can be solved for the spectrum of $\langle x_ix_j\rangle$ either by Fourier analysis (Schottky's method) or by computing the correlations $\langle x_i(t)x_j(t')\rangle$ from (1.1) with Ornstein's method.[9] In both cases one has to know *a priori* either the total variances $\langle x_ix_j\rangle$ or the spectrum of the quantities $\langle\epsilon_i\epsilon_j\rangle$. An example of the latter possibility was given by Petritz[10] and by van Vliet and Blok,[11] in the case of carrier fluctuations in photoconductors, where $\epsilon_i(t)$ represents the fluctuations in the incident photon stream, the spectrum of which is known from Bose-Einstein statistics. Our main conclusion here is that additional information is necessary in order to solve for the spectrum of the fluctuations from (1.1). Such information can in general be obtained from thermodynamical arguments or—in a purely statistical approach—from difference equations for the probability functions (Kolmogoroff[12]), integral equations (van Smoluchowski[13]) or partial differential equations (Fokker-Planck[13,14]).

In the present method, where we restrict ourselves to thermal equilibrium, the spectrum will be found directly, and the values of the variances $\langle x_ix_j\rangle$ have not to be known in advance but are obtained as a *result* by integration of the spectra. Again, we start from the kinetic equations; the main object now is to choose the extensive parameters x_i and the intensive parameters in such a way that they are conjugate in a thermodynamical sense. We then get the kinetic equations in a unified form. The introduction of noise source terms ϵ_i is not necessary. On the contrary, we impose a *macroscopic* perturbation $V_i(t)$ on the system where V_i has the dimension of the intensive variables. The response of $x_i(t)$ to this perturbation defines the admittances of the system, from which the spectral intensities of $\langle x_ix_j\rangle$ are found directly. This macroscopic approach validates the fact that noise spectra always only contain macroscopically observable quantities[15] (besides constants like e, k, etc.) which is not always recognized.

In accordance with the above remarks it is the author's feeling that many more applications of the fluctuation-dissipation theorem can be given than are known today. In the case of thermal noise in a resistor the application was straightforward, because the kinetic equation $R\dot{Q}=V$ is immediately of suitable form, since Q and V are conjugate quantities. In other cases, a transformation may be necessary. Finally we remark that the theorem also applies to cases which cannot be described with equations like (1.1), as long as the conjugate quantities can be defined.

2. Kinetic Equations and the Admittance Matrix

In what follows, an energy "state" will be defined either as a localized level in the forbidden gap or as a continuous band. The reasoning behind this is that the time for exchange of carriers in different energy levels within the conduction band or valence band is extremely short compared to the inverse of the frequencies in which we are interested. We shall consider the general case that s energy states $\mathcal{E}_1\cdots\mathcal{E}_s$ contribute to the carrier transitions, the number of electrons in the various states being $n_1\cdots n_s$. For consistency we shall deal with the electron occupancy in these states rather than the hole occupancy since that would lead to the introduction of ± signs in the results. It will be convenient to define the extensive variables as deviations from the equilibrium values (to which we assign the suffix 0)

$$\alpha_i=n_i-n_{i0}. \tag{2.1}$$

Since the total number of electrons is constant, we have the constraint

$$\sum_{i=1}^{s}\alpha_i=0. \tag{2.2}$$

Hence, the independent variables can be numbered as $\alpha_1\cdots\alpha_{s-1}$. To find the "thermodynamic forces" or conjugate variables to the α_i we can choose between the "free-energy language" or the "entropy language." Though both methods give the same results (see Appendix A) we prefer the first possibility which corresponds to the experimental condition that the crystal temperature is left constant. It is customary then to define the conjugate variables as the derivatives of the free energy with respect to $-\alpha$. In our case, however, a slight complication arises because of the constraint (2.2). To examine the situation we consider the free-energy total differential

$$dF=-TdS-PdV+\sum_{i=1}^{s}\mu_id\alpha_i=0, \tag{2.3}$$

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[8] K. M. van Vliet and J. Blok, Physica **22**, 231 (1956).

[9] L. S. Ornstein, Verslag. Gewone Vergader. Afdel. Natuurk. Koninkl. Ned. Akad. Wetenschap. **26**, 1005 (1917); Phys. Rev. **36**, 823 (1930).

[10] R. L. Petritz, Phys. Rev. **104**, 1508 (1956).

[11] K. M. van Vliet and J. Blok, Physica **22**, 525 (1956).

[12] A. N. Kolmogoroff, Math. Ann. **104**, 415 (1931).

[13] See M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945).

[14] A. D. Fokker, Ann. Physik **43**, 810 (1914); Arch. néerl. sci. **4**, 379 (1918).

[15] "Observable" means here that the quantities can be measured in principle. There may be practical limitations, however; e.g., carrier relaxation times smaller than 1 μsec cannot easily be measured with the normal techniques, whereas times of the order of 10^{-8} sec were found at this laboratory from noise spectra measurements.

with

$$\sum_{i=1}^{s} d\alpha_i = 0. \tag{2.4}$$

Here $\mu_i = \partial F^{(s)}/\partial \alpha_i$ is the chemical potential which in equilibrium ($\alpha_i = 0$) equals the Fermi level. [The superscript (s) means that F is considered as a function of all the variables $\alpha_1 \cdots \alpha_s$.] For a nonequilibrium state μ_i corresponds to the quasi-Fermi level for the charge carriers of group i (see Appendix A). The above equations can be rewritten as

$$dF = -TdS - PdV + \sum_{i=1}^{s-1} (\mu_i - \mu_s) d\alpha_i. \tag{2.5}$$

In accordance with this expression the thermodynamic forces are defined here as

$$X_i = -\partial F^{(s-1)}/\partial \alpha_i = \mu_s - \mu_i \quad (i = 1, 2 \cdots s-1), \tag{2.6}$$

where $F^{(s-1)}$ denotes F as a function of the independent variables only. The above definition states that the thermodynamic reaction forces in a nonequilibrium state which are responsible for the regression to equilibrium are the differences of the quasi-Fermi levels with respect to a reference state $\mathcal{E}_s$. One might wonder why these forces depend on the particular choice of s. The answer is that another set of forces $X_i' = \mu_p - \mu_i$ would give a completely equivalent description. Just as for chemical reactions[16] there are several other ways of choosing the X_i, e.g., $X_{ij}'' = \mu_i - \mu_j$ and cyclic, which introduces extraneous variables. We come back to this in the next section.

The generalized resistances are introduced as the proportionality constants which relate the forces and the fluxes or, in our case, relate the quasi-Fermi levels and the transition rates[17]

$$X_i = \sum_{j=1}^{s-1} R_{ij} \dot{\alpha}_j, \quad \text{or} \quad \dot{\alpha}_j = \sum_{k=1}^{s-1} (R^{-1})_{jk} X_k. \tag{2.7}$$

If we are close enough to equilibrium, the free energy may be expanded as

$$F(\alpha_1 \cdots \alpha_{s-1}) = \tfrac{1}{2} \sum_{i,j=1}^{s-1} \frac{\partial^2 F^{(s-1)}}{\partial \alpha_i \partial \alpha_j} \alpha_i \alpha_j = \tfrac{1}{2} \sum_{i,j=1}^{s-1} f_{ij} \alpha_i \alpha_j, \tag{2.8}$$

where

$$f_{ij} \equiv \{\partial^2 F^{(s-1)}/\partial \alpha_i \partial \alpha_j\}_{\alpha_i = \alpha_{i0}}.$$

Also, the X_i can be written as [compare (2.6)] $X_i = -\sum_j f_{ij} \alpha_j$, so that (2.7) results in the kinetic equations

$$\sum_{j=1}^{s-1} (R_{ij} \dot{\alpha}_j + f_{ij} \alpha_j) = 0. \tag{2.9}$$

The admittances are easily introduced in a statistical treatment[6] but its definition in a thermodynamic approach requires more care. Callen and Greene[5] hereto introduce an external driving system with which the system is in equilibrium if the two systems have equal values of their thermodynamic forces. To describe the nonequilibrium behavior, it is assumed that the driving system has an instantaneous response when its parameters are sinusoidally varied with an arbitrary frequency ω; i.e., that the system is at any time in quasi-static equilibrium and its forces are well defined. The forces of this driving system are called the driving forces. For low frequencies these driving forces which act on the original system balance the thermodynamic forces in the system. On a small time scale there will be a time lag of the reaction. This behavior can be described in terms of an admittance matrix Y_{ij}, introduced as follows. Let the driving forces be $V_i(t)$ and let

$$V_i(t) = \int_{-\infty}^{\infty} E_i(\omega) e^{j\omega t} d\omega, \tag{2.10a}$$

also

$$\alpha_i(t) = \int_{-\infty}^{\infty} \beta_i(\omega) e^{j\omega t} d\omega; \tag{2.10b}$$

then

$$j\omega \beta_i(\omega) = \sum_{j=1}^{s-1} Y_{ij}(\omega) E_j(\omega). \tag{2.11}$$

The procedure sketched above can easily be visualized in the case of fluctuations of the external parameters of a gas, enclosed by a diathermal piston and which is in equilibrium with a reservoir; then the pressure on the piston is the driving force. In our case it is not easy to assign a physical picture to the driving system. Nevertheless, the above idea leads to the conclusion that the generalized driving forces on which the definition of Y_{ij} is based are external force terms V_i, having the dimensions of quasi-Fermi levels, and which have to be added in the right-hand side of Eq. (2.9); i.e., the relation between, $\alpha_i(t)$ and $V_i(t)$ is

$$\sum_{j=1}^{s-1} (R_{ij} \dot{\alpha}_j + f_{ij} \alpha_j) = V_i(t), \tag{2.12}$$

or with (2.10) we get the "response equations"

$$\sum_{j=1}^{s-1} (R_{ij} j\omega \beta_j(\omega) + f_{ij} \beta_j(\omega) = E_i(\omega). \tag{2.13}$$

The theorem of Callen and Greene now gives a general relation between the conductance $\sigma_{ij} = \mathrm{Re}(Y_{ij})$ and the mean square fluctuations in the following form:

$$\langle \alpha_i \alpha_j \rangle \equiv \int_0^{\infty} G_{ij}(f) df = 4kT \int_0^{\infty} \sigma_{ij}(\omega) df/\omega^2, \tag{2.14}$$

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[16] S. R. de Groot, reference 2, Chap. 9.

[17] The $(R^{-1})_{ij}$ quantities are sometimes called conductances. This will not be done here since below we will introduce frequency-dependent conductances $\sigma_{ij}(\omega)$.

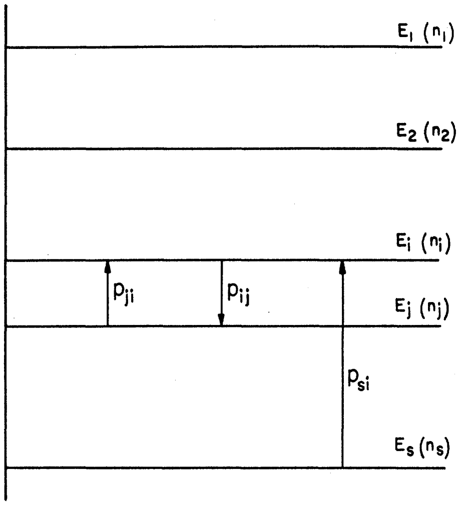

FIG. 1. Energy level diagram of arbitrary semiconductor.

where **G** is the spectral density matrix ($df=d\omega/2\pi$). The problem of finding G_{ij} is thus reduced to finding the admittance Y_{ij}. For this in turn we need the knowledge of R_{ij} and f_{ij}. The latter quantities are found in a straightforward way (see Appendix A). The R_{ij} will be derived in the next section.

3. The Generalized Resistances and the Lifetimes

In what follows, we shall assume that the semiconductor is nondegenerate. The extension to degenerate cases is treated in Appendix B.

The R_{ij} follow easily from their definition (2.7) and the expression for the forces (2.6). Suppose we change the Fermi levels by some means from μ_0 to μ_i. Let us furthermore denote the transitions per second of electrons from $\mathcal{E}_i$ to $\mathcal{E}_j$ by p_{ij} (see Fig. 1), such that

$$p_{ij}=\gamma_{ij}n_i(N_j-n_j), \tag{3.1}$$

where γ_{ij} is a proportionality constant,[18] depending on the cross section for this particular transition and where n_i is the number of electrons available in the state $\mathcal{E}_i$ and N_j-n_j is the number of holes present in $\mathcal{E}_j$. Since the generation of carriers to $\mathcal{E}_i$ equals $\sum'_{j=1}{}^s p_{ji}$ and the recombination equals $\sum'_{j=1}{}^s p_{ij}$ (where the prime denotes that $i=j$ has to be excluded), the net rate of change of n_i is

$$\dot{\alpha}_i=\sum_{j=1}^{s}{}' (p_{ji}-p_{ij}). \tag{3.2}$$

Using (3.1) and the expression (A.8) of Appendix A, we obtain

$$\begin{aligned}\dot{\alpha}_i=\sum_{j=1}^{s}{}'\gamma_{ji}&\frac{N_j}{1+\exp[(\mathcal{E}_j-\mu_j)/kT]}\\ &\times\frac{N_i}{1+\exp[(-\mathcal{E}_i+\mu_i)/kT]}\\ &-\sum_{j=1}^{s}{}'\gamma_{ij}\frac{N_i}{1+\exp[(\mathcal{E}_i-\mu_i)/kT]}\\ &\times\frac{N_j}{1+\exp[(-\mathcal{E}_j+\mu_j)/kT]}.\end{aligned} \tag{3.3}$$

We then expand the right-hand side for small $\mu_i-\mu_0$ in a Taylor series. The lengthy expression, so obtained can be considerably simplified by noting that the principle of detailed balance tells us that the equilibrium rates $p_{ij}{}^0$ and $p_{ji}{}^0$ are equal, i.e.,

$$\begin{aligned}p_{ij}{}^0=\gamma_{ij}&\frac{N_i}{1+\exp[(\mathcal{E}_i-\mu_0)/kT]}\\ &\times\frac{N_j}{1+\exp[(-\mathcal{E}_j+\mu_0)/kT]}\\ =\gamma_{ji}&\frac{N_j}{1+\exp[(\mathcal{E}_j-\mu_0)/kT]}\\ &\times\frac{N_i}{1+\exp[(-\mathcal{E}_i+\mu_0)/kT]}=p_{ji}{}^0.\end{aligned} \tag{3.4}$$

We then find that

$$\dot{\alpha}_i=\sum_{j=1}^{s}{}' p_{ij}{}^0(\mu_j-\mu_i)/kT. \tag{3.5}$$

If one or both of the states $\mathcal{E}_i$ and $\mathcal{E}_j$ would represent a band instead of a localized level, then (3.3) has to be changed since we must use the expressions (A.11) and (A.12) of Appendix A instead of (A.8). One easily shows, however, that this also results in (3.5) which therefore holds generally. From (2.6) and (2.7) we also have

$$\dot{\alpha}_i=\sum_{j=1}^{s-1}(R^{-1})_{ij}(\mu_s-\mu_j). \tag{3.6}$$

To compare the coefficients we write (3.5) and (3.6) as follows:

$$kT\dot{\alpha}_i=\sum_{j=1}^{s-1}{}' p_{ij}{}^0\mu_j-(\sum_{j=1}^{s}{}' p_{ij}{}^0)\mu_i+p_{is}{}^0\mu_s, \tag{3.5a}$$

$$\dot{\alpha}_i=-\sum_{j=1}^{s-1}{}'(R^{-1})_{ij}\mu_j-(R^{-1})_{ii}\mu_i+[\sum_{j=1}^{s-1}(R^{-1})_{ij}]\mu_s. \tag{3.6a}$$

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[18] If $\mathcal{E}_i$ and $\mathcal{E}_j$ are both localized impurity levels which do not occur in great abundance, γ_{ij} and γ_{ji} are approximately zero. Since this does not simplify the general expressions we shall take all p_{ij} along.

Comparison of the first two terms on the right-hand side gives

$$\begin{aligned}(R^{-1})_{ij} &= -p_{ij}{}^0/kT \quad (i\neq j;\, i,\, j=1,\, \cdots s-1),\\ (R^{-1})_{ii} &= \sum_{j=1}^{s}{}' p_{ij}{}^0/kT \quad (i=1,\, 2\cdots s-1),\end{aligned} \tag{3.7}$$

whereas comparison of the coefficients of μ_s leads to

$$\sum_{j=1}^{s-1} (R^{-1})_{ij} = p_{is}{}^0/kT,$$

which is consistent with (3.7). In this way the reciprocal generalized resistances have been expressed in the transition probabilities.

In Eqs. (3.7) the effect of the asymmetry with respect to the level $\mathcal{E}_s$ manifests itself only in the diagonal elements, which would have been zero in a symmetrical treatment. A completely similar situation exists in electrical n-terminal networks where one of the junctions is used as a reference junction such that the independent potentials are the voltage differences with respect to the potential of this junction. Actually, Shockley and Read[19] already pointed out for the particular recombination process considered by them that the μ's can be looked upon as voltages and the $\dot{\alpha}$'s as currents. In Sec. 6 we extend this idea and present an equivalent electrical network.

From (3.7) we see that $R_{ij}=R_{ji}$, since $p_{ij}{}^0=p_{ji}{}^0$. This means that the Onsager relations in our case are a direct consequence of the principle of detailed balance. In photoconductors the latter principle does not hold and cyclic transitions can occur under illumination. This is the reason that the results in photoconductors, where the above theory does not apply, are so much more complicated.

Next we shall find the relaxation times characteristic for the return to equilibrium. We write (2.9) in the form

$$\dot{\alpha}_j = -\sum_{l,k=1}^{s-1} (R^{-1})_{jk} f_{kl} \alpha_l. \tag{3.8}$$

A particular solution of (3.8) is $A\exp(-t/\tau_k)$. Substituting this we find that there are $s-1$ relaxation times which are the inverse eigenvalues of $\mathbf{R}^{-1}\mathbf{f}$, i.e.,

$$|\mathbf{R}^{-1}\mathbf{f} - (1/\tau_k)\mathbf{I}| = 0, \tag{3.9}$$

where $\mathbf{I}$ is the unit matrix. In this way the τ's are expressed in the R_{ij} and f_{ij}. We note, however, that the matrix $\mathbf{a}\equiv -\mathbf{R}^{-1}\mathbf{f}$ can also be found directly from the transition rates p_{ij}. To show this we develop p_{ij} according to

$$p_{ij} = \sum_{l=1}^{s-1} (\partial p_{ij}/\partial\alpha_l)_0 \alpha_l + p_{ij}{}^0.$$

Equations (3.2) then give

$$\dot{\alpha}_i = \sum_{l=1}^{s-1} \sum_{j=1}^{s}{}' (\partial p_{ji}/\partial\alpha_l - \partial p_{ij}/\partial\alpha_l)_0 \alpha_l, \tag{3.10}$$

and comparison with (3.8) yields

$$a_{il} = -(\mathbf{R}^{-1}\mathbf{f})_{il} = \sum_{j=1}^{s}{}' (\partial p_{ji}/\partial\alpha_l - \partial p_{ij}/\partial\alpha_l)_0. \tag{3.11}$$

Equations (3.10) and (3.11) were the basis of the statistical procedure followed before[8] (see also Sec. 8).

4. Application to Simple Intrinsic and Extrinsic Semiconductors

Before proceeding to complicated systems, we shall first illustrate the theory in the simple case in which there is only one independent variable, i.e., the transitions of interest will occur between two energy states only. These two states may be the conduction band and the valence band (intrinsic or nearly intrinsic semiconductors), the conduction band and donor levels (n-type semiconductors), minority-carrier traps and valence band, etc. The one variable equations for the response (2.13), for the admittance (2.11), for R (3.7) and for τ (3.9) are, respectively:

$$\beta(\omega)(Rj\omega+f) = E(\omega) \tag{4.1}$$

$$j\omega\beta(\omega) = Y(\omega)E(\omega), \tag{4.2}$$

$$R = kT/g_0 = kT/r_0, \tag{4.3}$$

$$\tau = R/f. \tag{4.4}$$

Here $g_0\equiv p_{21}{}^0$ is the equilibrium generation rate and $r_0\equiv p_{12}{}^0$ is the equilibrium recombination rate. Equations (4.1) and (4.2) yield

$$Y = \frac{j\omega}{f+j\omega R}; \quad \sigma = \frac{\omega^2 R}{f^2+\omega^2 R^2}. \tag{4.5}$$

Hence the spectrum is

$$G_\alpha(f) = 4kTR/(f^2+\omega^2R^2). \tag{4.6}$$

Using (4.3) and (4.4), we can bring this from the "Nyquist form" (4.6) into the more familiar form

$$G_\alpha(f) = 4g_0\tau^2/(1+\omega^2\tau^2). \tag{4.7}$$

This formula is identical with a result found before [reference 8, Eq. (17c)]. Apparently the result (4.7) is more general than other expressions obtained before.[8] We will see in Appendix B that it is *even valid for degenerate semiconductors*. Equation (4.7) does not refer anymore to the thermodynamical basis on which it was derived. Results for particular applications can be found by calculating τ from the thermodynamical expression (4.4) or from the derivatives of the various transition rates [compare end of the preceding section;

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[19] W. Shockley and W. T. Read, Phys. Rev. 87, 835 (1952).

for one variable, see reference 8, Eq. (15)]. Although the latter procedure is much faster, we shall apply the thermodynamical expression (4.4) in the two examples given below in order to corroborate the method.

As a first example consider a nearly intrinsic n-type semiconductor (all donors are assumed to be ionized). For the free-energy second derivative, we have in this case [see Appendix (A.13)] $f=kT(1/n_0+1/p_0)$. Hence, from (4.4) and (4.3):

$$1/\tau=g_0(1/n_0+1/p_0), \tag{4.8}$$

which is van Roosbroeck's result for direct recombination of electrons with holes in the valence band.[20] Consequently, (4.7) can also be written as

$$G_\alpha(\text{nearly intr.})=4\frac{n_0p_0}{n_0+p_0}\left(\frac{\tau}{1+\omega^2\tau^2}\right). \tag{4.9}$$

To find the current noise we note that $i(t)=e\mu_n n(t)E/L+e\mu_p p(t)E/L$, or $\langle\Delta i(t)^2\rangle=e^2\mu_p^2(1+b)^2\langle\alpha^2\rangle E^2/L^2$ where L is the length of the crystal and $b=\mu_n/\mu_p$. Using (4.9), we obtain for the spectral intensity $G_i(f)$ of $\langle\Delta i^2\rangle$

$$G_i(\text{nearly intr.})=4\langle i^2\rangle\frac{(b+1)^2n_0p_0}{(bn_0+p_0)^2(n_0+p_0)}\left(\frac{\tau}{1+\omega^2\tau^2}\right). \tag{4.10}$$

For an intrinsic semiconductor this results in

$$G_i(\text{intrinsic})=2i^2\tau/n_0(1+\omega^2\tau^2). \tag{4.11}$$

Secondly, consider an extrinsic semiconductor (e.g., n-type) in which the donors N_D are only partially ionized. For τ we find from (4.4), applying (A.14) of Appendix A,

$$\frac{1}{\tau}=g_0\left(\frac{2}{n_0}+\frac{1}{N_D-n_0}\right), \tag{4.12}$$

similar to (4.8). Accordingly, (4.7) can be written

$$G_\alpha(f)=\frac{4n_0(N_D-n_0)\tau}{(2N_D-n_0)(1+\omega^2\tau^2)}. \tag{4.13}$$

Since $i=e\mu_n nE/L$, we find

$$G_i(\text{extrinsic})=\frac{4i^2(N_D-n_0)\tau}{n_0(2N_D-n_0)(1+\omega^2\tau^2)}. \tag{4.14}$$

Another case, encountered experimentally,[21] is one in which trapping occurs. If the trapping center interacts only with either the conduction band or the valence band, then (4.7) can be applied. If the trap, however, acts as a recombination center, there are two variables and we get much more complicated results. This case is treated in Sec. 7. The same is true for semiconductors with both intrinsic and extrinsic transitions. We then need the general results of the next section.

5. General Solution

The reciprocal admittance matrix is easily found. Equation (2.11) gives

$$E_i(\omega)=\sum_{j=1}^{s-1} j\omega(Y^{-1})_{ij}\beta_j(\omega). \tag{5.1}$$

Comparison with (2.13) yields

$$\mathbf{Y}^{-1}=\mathbf{R}+\mathbf{f}/j\omega, \tag{5.2}$$

and consequently the spectral densities can be expressed by the matrix equation

$$\mathbf{G}=4kT\,\mathrm{Re}\{(\mathbf{R}+\mathbf{f}/j\omega)^{-1}\}\omega^{-2}.$$

Unfortunately this solution does not give us any insight into the nature of the solution. We therefore shall obtain some other expressions. By inverting (2.13), we have

$$j\omega\beta_j=\sum\nolimits_k a_{jk}\beta_k+(R^{-1})_{jk}E_k, \tag{5.3}$$

where, as before, $\mathbf{a}=-\mathbf{R}^{-1}\mathbf{f}$. We now make the transformation $\beta_j'=\sum_l c_{jl}\beta_l$, where $\mathbf{c}$ makes $\mathbf{a}'=\mathbf{cac}^{-1}$ a diagonal matrix. Equation (5.3) then transforms, if we also write $E_j'=\sum_l c_{jl}E_l$ and $(\mathbf{R}^{-1})'=\mathbf{c}(\mathbf{R}^{-1})\mathbf{c}^{-1}$, into

$$j\omega\beta_k'=-\frac{1}{\tau_k}\beta_k'+\sum\nolimits_l(R^{-1})_{kl}'E_l', \tag{5.4}$$

where the lifetimes were introduced from (3.9). Since also $j\omega\beta_k'=\sum_l Y_{kl}'E_l'$, where $\mathbf{Y}'$ is the transformed admittance matrix, we have

$$\begin{gathered}Y_{kl}'=(R^{-1})_{kl}'j\omega\tau_k/(1+j\omega\tau_k),\\ \text{or}\\ \sigma_{kl}'=(R^{-1})_{kl}'\omega^2\tau_k^2/(1+\omega^2\tau_k^2).\end{gathered} \tag{5.5}$$

Writing now $(\mathbf{R}^{-1})'=\mathbf{c}(\mathbf{R}^{-1})\mathbf{c}^{-1}$ and $\boldsymbol{\sigma}=\mathbf{c}^{-1}\boldsymbol{\sigma}'\mathbf{c}$, we obtain

$$G_{mn}=4kT\sigma_{mn}/\omega^2=4kT\sum_{i,k=1}^{s-1}(c^{-1})_{mk}c_{ki}(R^{-1})_{in}\tau_k^2\times(1+\omega^2\tau_k^2)^{-1}. \tag{5.6}$$

This is the Nyquist form. Using (3.7) we can express G_{mn} in terms of the transition rates directly:

$$G_{mn}=4\sum_{k=1}^{s-1}\sum_{i\neq n}^{s}(c^{-1})_{mk}p_{in}^0(c_{kn}-c_{ki})\tau_k^2/(1+\omega^2\tau_k^2), \tag{5.7}$$

where we define $c_{ks}\equiv 0$ for all k.

We finally will derive the result for $\langle\alpha_n\alpha_m\rangle$ from the spectra. We thereto note that, according to the definition of $\mathbf{c}$,

$$\sum\nolimits_i c_{ki}a_{il}=-(1/\tau_k)c_{kl}, \tag{5.8}$$

or

$$\sum\nolimits_{i,j}c_{ki}(R^{-1})_{ij}f_{jl}=(1/\tau_k)c_{kl},$$

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[20] W. van Roosbroeck and W. Shockley, Phys. Rev. **94**, 1558 (1954).

[21] H. A. Gebbie, Phys. Rev. **98**, 1567 (1955).

or

$$\sum_i c_{ki}(R^{-1})_{in}=\sum_l (1/\tau_k)c_{kl}(f^{-1})_{ln}. \tag{5.9}$$

Substitution of this in (5.6) yields the result

$$\langle\alpha_n\alpha_m\rangle=\int_0^\infty\left(\frac{2}{\pi}\right)kT\sum_{k,l=1}^{s-1}(c^{-1})_{mk}c_{kl}(f^{-1})_{ln}\tau_k \times(1+\omega^2\tau_k^2)^{-1}d\omega$$

$$=kT\sum_{k,l=1}^{s-1}(c^{-1})_{mk}c_{kl}(f^{-1})_{ln}=kT(f^{-1})_{mn}. \tag{5.10}$$

This is in complete agreement with the results of statistical thermodynamics (see Appendix A).

Moreover, the expressions (5.6) and (5.7) show clearly that the spectra will be always rather smooth and never exhibit "resonances" (maxima or minima). The general aspect of the solution is pictured in Fig. 2. The cross-correlation spectra ($m\neq n$) may show sharp cutoffs (compare Sec. 7).

6. Electrical Analogs

Consider an s terminal network, connected by conductances $g_{ij}=p_{ij}^0/kT$ (Fig. 3). Suppose that at a certain instant voltages $V_1\cdots V_s$ are applied to the terminals; the junction s will be taken as the datum junction. The total current through all the resistance branches that have junction j in common, and directed toward this junction will be i_j. The nodal network equations are then

$$-i_j=\sum_{k=1}^{s-1}(R^{-1})_{jk}(V_k-V_s), \tag{6.1}$$

where the "comitances" $(R^{-1})_{jk}$ satisfy (3.7) according to a well-known circuitry result.[22] Equation (6.1) is identical with (3.6) if the V_i correspond to the quasi-Fermi levels μ_i and the currents i_j to $\dot{\alpha}_j$. Each junction in Fig. 2 corresponds to a particular energy state.

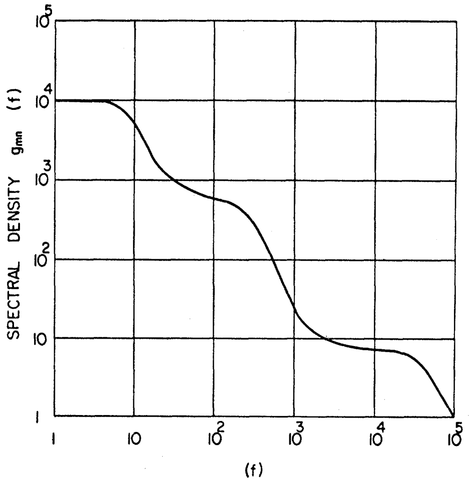

FIG. 2. General aspect of the many-level problem.

When we next consider the regression of the current to zero when the system is left to itself (the voltages are taken away at $t=0$), then we have to introduce capacitors which account for the slow way the charges (concentrations α_j) leak away. Since the carrier rate $\dot{\alpha}_i$ is effected by a change in the Fermi level μ_j, we must introduce both self capacitances C_{ii} and mutual capacitances C_{ij}; we will find it convenient to also introduce the reciprocal capacitances or elastances $d_{ij}=(C^{-1})_{ij}$. Taking $d_{ij}\equiv f_{ij}$ the transient behavior of the semiconductor is equal to that of the network of Fig. 4. To prove this we note that $V_k=\sum_l f_{kl}\int i_l dt$ where i_l as before is the sum of the currents through the conductances at junction l. Hence, from (6.1),

$$\sum_k\left(R_{jk}i_k+f_{jk}\int i_k dt\right)=0 \tag{6.2}$$

in accordance with (2.9).

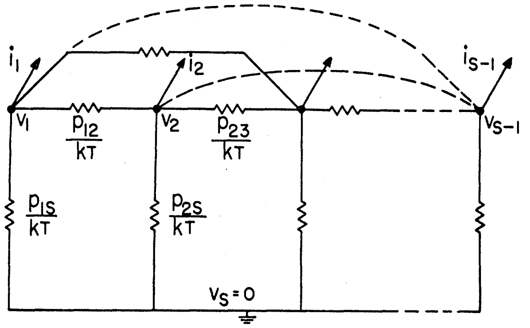

FIG. 3. Dc equivalent electrical network.

Finally the response to the driving forces E_j can also be found from the network, if we include voltage generators E_i-E_j between each pair of junctions i and j.

A similar network analog has been proposed by North.[23] This is simpler than the one given here since it contains no mutual capacitances whereas there is complete symmetry between all the levels $\mathcal{E}_1\cdots\mathcal{E}_s$. It is expected that such a network can be obtained from the above one by a proper network transformation. Although North's network is more suitable for practical calculation, the above network is a direct picture of the theory presented before. The resolution into the natural modes is also analogous to the general solution of the previous section.

7. Application to the Shockley-Read Model

We consider a semiconductor in which all donors are ionized (or all acceptors filled) and which contains one

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[22] See, e.g., H. W. Bode, *Network Analysis and Feedback Amplifier Design* (D. Van Nostrand Company, Inc., Princeton, 1945), Chap. 1.

[23] D. O. North (private communication); see also Bull. Am. Phys. Soc. Ser. II, 2, 319 (1957).

kind of recombination center. This is the picture that Shockley and Read[19] proposed for Ge and Si at sufficiently high temperatures. We consider the fluctuations in the rates p_{13}, p_{31}, p_{23}, p_{32} between the conduction band, valence band, and the centers, whose energy states, respectively, will be labelled $\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$. The direct transitions p_{12} and p_{21} are very rare in these materials and will consequently be neglected. As independent variables we consider n and $-p$. Denoting the number of recombination centers by N, the number of electrons in these states by i, and the number of ionized donors by N_D, the consraint is (assuming all centers N to be filled at $T=0$) $n+i-p=N+N_D$. The transition probabilities are

$$\begin{aligned} p_{31}&=\gamma i=\gamma(N+N_D+p-n),\\ p_{13}&=\delta n(N-i)=\delta n(-N_D+n-p),\\ p_{23}&=\epsilon(N-i)=\epsilon(-N_D+n-p),\\ p_{32}&=\kappa ip=\kappa p(N+N_D+p-n),\end{aligned} \tag{7.1}$$

where γ, δ, ϵ and κ are transition constants. The generalized resistances are

$$\begin{aligned} (R^{-1})_{11}&=(\tau_{n0}N)^{-1}n_0(N-i_0)/kT,\\ (R^{-1})_{22}&=(\tau_{p0}N)^{-1}p_0i_0/kT,\\ (R^{-1})_{12}&=(R^{-1})_{21}=0,\end{aligned} \tag{7.2}$$

where we introduced the Shockley-Read symbols $\tau_{n0}=(\delta N)^{-1}$ and $\tau_{p0}=(\kappa N)^{-1}$. The transition rates are then given by two simultaneous differential equations of the form (3.10).[24] The matrix **a** is found to be, from (3.11) and (7.1),

$$\mathbf{a}=-\left\|\begin{matrix} (N\tau_{n0})^{-1} & (N\tau_{n0})^{-1}(n_0+n_1)\\ \quad\times(n_1+n_0+N-i_0) & \\ (N\tau_{p0})^{-1}(p_0+p_1) & (N\tau_{p0})^{-1}\\ & \quad\times(p_0+p_1+i_0)\end{matrix}\right\|. \tag{7.3}$$

Here we introduced

$$\begin{aligned} n_1&=n_0(N-i_0)/i_0=C\exp(\mathcal{E}_3-\mathcal{E}_1)/kT,\\ p_1&=i_0p_0/(N-i_0)=C'\exp(\mathcal{E}_2-\mathcal{E}_3)/kT,\end{aligned} \tag{7.4}$$

where C and C' are constants. The two relaxation times τ_1 and τ_2 are the reciprocal eigenvalues of (7.3). For the case in which the number of recombination centers is much less than the number of majority carriers, one can easily show that $\tau_1\approx\tau_{\mathrm{SR}}$, $\tau_2\ll\tau_1$, where τ_{SR} is the Shockley-Read lifetime. From (3.9), we have

$$1/\tau_{1,2}=-\tfrac{1}{2}(a_{11}+a_{22})\{1\pm[1-4\Delta/(a_{11}+a_{22})^2]^{\frac{1}{2}}\}, \tag{7.5}$$

where $\Delta=a_{11}a_{22}-a_{12}a_{21}$.

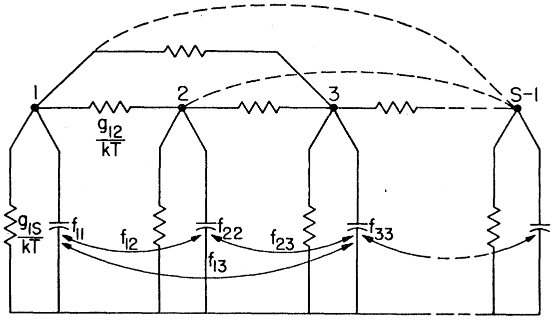

FIG. 4. Ac equivalent electrical network.

For $N\ll n$, and $i\lesssim p$, the square root can be expanded and we have

$$\tau_1\approx-(a_{11}+a_{22})/\Delta. \tag{7.6}$$

If one writes[25] $i_0=N(1+n_1/n_0)^{-1}$, $N-i_0=N(1+n_0/n_1)^{-1}$, it is easily found that $\Delta\approx(\tau_{n0}\tau_{p0}N)^{-1}(n_0+p_0)$. Then (7.6) results in

$$\tau=\{\tau_{n0}(p_0+p_1)+\tau_{p0}(n_0+n_1)\}/(n_0+p_0), \tag{7.7}$$

which is the Shockley-Read expression. Since now $\Delta i\approx 0$ and $\Delta p\approx\Delta n$, this case has been reduced to a one-variable problem. Carrying through the approximations [using Eq. (7.9) given below], one arrives at the simple result (4.10) with the only difference that now τ is given by (7.7) instead of (4.8).

In the more general case large deviations can occur. We calculate the noise from (5.7), the **c** matrix being

$$\mathbf{c}=\left\|\begin{matrix} a_{21} & -a_{11}-1/\tau_1\\ a_{21} & -a_{11}-1/\tau_2\end{matrix}\right\|. \tag{7.8}$$

Substituting this into (5.7), we obtain (denoting by G_{nn}, G_{pp}, and G_{np} the spectral densities of $\langle\Delta n^2\rangle$, $\langle\Delta p^2\rangle$ and $\langle\Delta n\Delta p\rangle$, respectively),

$$G_{nn}=\sum_{1,2}\frac{4\tau_1^2}{1+\omega^2\tau_1^2}\,\frac{\tau_1(a_{11}\tau_2+1)n_0(N-i_0)}{(\tau_1-\tau_2)\tau_{n0}N}, \tag{7.9}$$

$$G_{pp}=\sum_{1,2}\frac{4\tau_1^2}{1+\omega^2\tau_1^2}\,\frac{\tau_2(a_{11}\tau_1+1)p_0i_0}{(\tau_2-\tau_1)\tau_{p0}N}, \tag{7.10}$$

$$G_{np}=\sum_{1,2}\frac{4\tau_1^2}{1+\omega^2\tau_1^2}\,\frac{\tau_1\tau_2a_{21}n_0(N-i_0)}{(\tau_2-\tau_1)\tau_{n0}N}, \tag{7.11}$$

where $\sum_{1,2}$ means that a similar term, in which τ_1 and τ_2 are interchanged, has to be added. These expressions, together with (7.3) and (7.5) give the complete solution. From Eqs. (7.11) we see that the two terms of the right-hand side for $\omega\tau_2\gg 1$ (supposing τ_2 to be the smallest relaxation time) are equal in magnitude but opposite in sign. This means that $G_{np}=0$ for $\omega\tau_2\gg 1$. Hence, for sufficiently high frequencies the interaction of the holes and of the electrons

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[24] D. J. Sandiford, Phys. Rev. **105**, 524 (1957). In this paper it is also pointed out that the Shockley-Read theory does not give the transient lifetimes for added current carriers with which we are concerned here, but instead deals with the steady state lifetimes for added current carriers.

[25] F. W. G. Rose and D. J. Sandiford, Proc. Phys. Soc. (London) **B68**, 894 (1955).

with the recombination centers can be considered to be independent.

To demonstrate the effect of the number of recombination centers upon the noise, we calculated the noise for the following two cases:

(a) $n_0=10\times10^{13}$ cm^{-3}, $p_0=0.8\times10^{13}$ cm^{-3},
$N_D=9\times10^{13}$ cm^{-3}, $N=0.3\times10^{13}$ cm^{-3},
$\tau_{n0}=\tau_{p0}=10^{-5}$ sec, $\mu_n=\mu_p$.

(b) n_0, p_0, N_D, τ_{n0}, τ_{p0} as above,
$N=30\times10^{13}$.

From (7.4), n_1 and p_1 follow, and from (7.3) the a's. For case (a) the current noise was calculated from (4.10). In case (b) we must use the more general relation between the spectral density G_i of $\langle\Delta i^2\rangle$ and the spectral densities of the carrier variances

$$G_i=\frac{i^2}{(bn_0+p_0)^2}\{b^2G_{nn}+2bG_{np}+G_{pp}\}. \qquad (7.12)$$

The results are shown in Fig. 5; curve I represents case (a), curve II case (b). It is seen that in case (b) the time constants are quite different from (7.7). At high frequencies a second bump appears. It might be possible that in other cases this bump will be more pronounced than in our numerical example. Experimentally two-bump spectra are only seldom encountered in germanium although an indication was found by Hyde.[26] Obviously, one reason is that in most cases thermal noise predominates at high frequencies. Often, a slope less than two for $\omega\tau\gg1$ is observed. It is not likely that this is caused by an overlap of the two bumps involved here, since our τ_1 and τ_2 will always be rather far apart. It is believed, however, that such a spectrum is caused by a slight spreading in energy depth of the recombination levels.

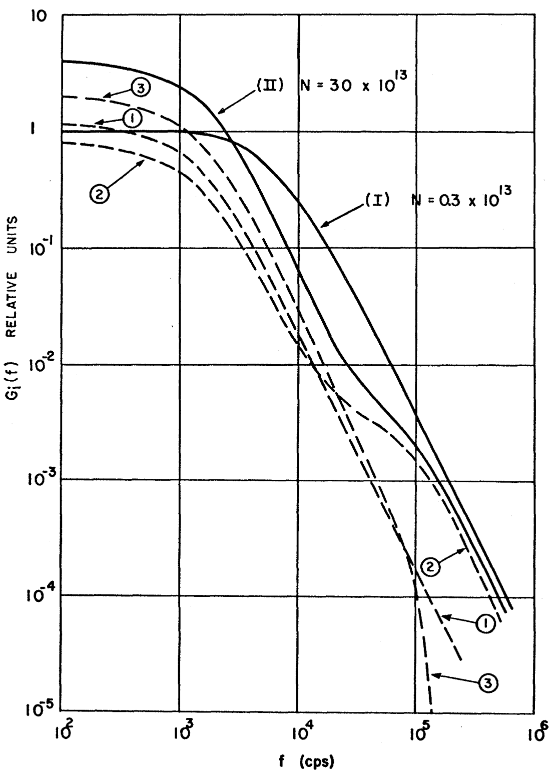

FIG. 5. Effect of the density of recombination centers on the noise of near-intrinsic material (calculated according to Sec. 7). 1. Contribution of G_{nn} to II. 2. Contribution of G_{pp} to II. 3. Contribution of G_{np} to II. Note the steep cutoff.

8. Comparison with Statistical Results

(*a*) *The variances.*—In Sec. 5 and in Appendix A we derived a thermodynamic expression for the variances:

$$\langle\boldsymbol{\alpha}\boldsymbol{\alpha}\rangle=kT\mathbf{f}^{-1}, \qquad (8.1)$$

where $\langle\boldsymbol{\alpha}\boldsymbol{\alpha}\rangle$ means the matrix with elements $\langle\alpha_i\alpha_j\rangle$. In a statistical procedure these variances are not so easily found. For one variable Burgess found a general expression for $\langle\alpha^2\rangle$ expressed in terms of the generation and recombination rates (so-called *g-r* theorem[27]). Van Vliet and Blok[8] obtained an extension of this theorem for more variables in a matrix form by solving the Fokker-Planck equation. The generalized *g-r* theorem reads:

$$\mathbf{a}\langle\boldsymbol{\alpha}\boldsymbol{\alpha}\rangle+\langle\boldsymbol{\alpha}\boldsymbol{\alpha}\rangle\mathbf{a}^T=-\mathbf{B}. \qquad (8.2)$$

Here $\mathbf{a}$ is the "*g-r* matrix" given by (3.11), $\mathbf{a}^T$ is the transposed matrix, whereas $\mathbf{B}$ is composed of the second-order moments of the Fokker-Planck equation, given in reference 8, Eq. (27):

$$B_{ii}=2\sum_{k=1}^{s}{}' p_{ik}^0, \quad B_{ij}=-p_{ij}^0-p_{ji}^0 \quad (i\neq j). \qquad (8.3)$$

The solution (8.1) is so completely different in form from (8.2) that at first it could hardly be believed that the results should be identical. Later on, for the particular case of a one impurity level semiconductor the equivalence was proven by means of lengthy algebraic manipulations.[28] Now, however, we are in a position to prove the equivalence directly. The link between the two procedures is expressed by the relations

$$\mathbf{a}=-\mathbf{R}^{-1}\mathbf{f}, \qquad (8.4a)$$

$$\mathbf{B}=2kT\mathbf{R}^{-1}, \qquad (8.4b)$$

where the first relation was stated in Sec. 3 whereas the latter one follows from a comparison of (3.7) and (8.3). Multipling (8.1) with $\mathbf{R}^{-1}\mathbf{f}$ from the left, we find, using (8.4a), that $\mathbf{a}\langle\boldsymbol{\alpha}\boldsymbol{\alpha}\rangle=-kT\mathbf{R}^{-1}$, or with

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[26] F. J. Hyde, *Report of the Conference of the Physical Society on Semiconductors, Rugby, England, 1956*, pages 57–64.

[27] R. E. Burgess, Physica **20**, 1007 (1954); Proc. Phys. Soc. (London) **B69**, 1020 (1956).

[28] K. M. van Vliet, Physica **23**, 248 (1957).

(8.4b) $\mathbf{a}\langle\boldsymbol{\alpha\alpha}\rangle=-\mathbf{B}/2$. Likewise, multiplying (8.1) through with $\mathbf{fR}^{-1}$, we find (noting that $\mathbf{a}^T=-\mathbf{f}^T(\mathbf{R}^T)^{-1}=-\mathbf{fR}^{-1}$) the result $\langle\boldsymbol{\alpha\alpha}\rangle\mathbf{a}^T=-\mathbf{B}/2$. Hence, Eq. (8.2) is vindicated. We also see that—because of detailed balance—the two terms on the left-hand side of Eq. (8.2) are equal. In photoconductors we do not expect such a simplification.

(*b*) *The spectra.*—Using the Langevin equations [see (1.1)] and the variances from (8.2), we have also computed the spectra with Ornstein's method. The expressions so obtained contain the elements B_{ij}. The equivalence with (5.6) can again easily be established, by employing (8.4a) and (8.4b).

CONCLUSIONS

The formalism of irreversible thermodynamics applied to semiconductor carrier transitions constitutes a very general way to compute carrier density fluctuations. It puts the kinetic equations, relating the forces and the fluxes in a unified form, so that the generalized Nyquist theorem becomes applicable. This is illustrated for single and more variable cases. An attractive feature is that the variances have not to be known in advance but are obtained as a consequence of the spectral intensities. The method is essentially a macroscopic one since no noise sources enter into the calculations: on the contrary the main object is to find the admittances for the perturbed state. Moreover, the procedure gives a complete link between thermodynamical and statistical theories, published before.

ACKNOWLEDGMENTS

The author wishes to express his thanks to Dr. A. van der Ziel for his interest in this work. He also wants to acknowledge discussions with Dr. D. O. North and Dr. R. E. Burgess, which resulted from a talk on this subject for the American Physical Society held in Boulder, Colorado, September, 1957.

APPENDIX A. SOME RESULTS OF STATISTICAL THERMODYNAMICS

In this Appendix we shall include some results,[29–32] well-known in statistical thermodynamics, for the sake of completeness of the text.

Let the entropy function be $S(\alpha_1\cdots\alpha_{s-1})$ and let the distribution function for the α_i be $W(\alpha_1\cdots\alpha_{s-1})$; then, according to the Boltzmann-Einstein theorem,

$$S(\alpha_1\cdots\alpha_{s-1})=k\ln W(\alpha_1\cdots\alpha_{s-1})+C, \qquad (A.1)$$

where C is a normalization constant. Expanding the entropy, we have, if $s_{ij}\equiv-(\partial^2S/\partial\alpha_i\partial\alpha_j)_0$,

$$W(\alpha_1\cdots\alpha_{s-1})=C'\exp\left(-\frac{1}{2k}\sum_{i,j}s_{ij}\alpha_i\alpha_j\right). \qquad (A.2)$$

This is a multivariate normal distribution for which the general result holds[29]:

$$\langle\alpha_i\alpha_j\rangle=k(s^{-1})_{ij}, \qquad (A.3)$$

where $\mathbf{s}^{-1}$ is the reciprocal matrix of $\mathbf{s}$. Since the free energy $F=\sum_i\mathcal{E}_in_i-TS$, we find that $f_{ij}\equiv(\partial^2F/\partial\alpha_i\partial\alpha_j)_0=Ts_{ij}$; hence we can write alternatively:

$$\langle\alpha_i\alpha_j\rangle=kT(f^{-1})_{ij}, \qquad (A.4)$$

in accordance with Sec. 5.

To actually calculate F and its derivatives, we start with the thermodynamic probability for a macrostate Ω_i in which n_i electrons are distributed over N_i levels of energy $\mathcal{E}_i$:

$$\Omega_i=N_i!/n_i!(N_i-n_i)!. \qquad (A.5)$$

For the free energy F_i associated with the carriers n_i, we find $F_i=n_i\mathcal{E}_i-kT\ln\Omega_i$, or, using Stirling's approximation,

$$F_i=n_i\mathcal{E}_i-kT\{N_i\ln N_i-n_i\ln n_i-(N_i-n_i)\ln(N_i-n_i)\}. \qquad (A.6)$$

For a nonequilibrium state $dF_i/dn_i=\mu_i\neq\mu_j$, etc. Equation (A.6) yields

$$\mu_i=\mathcal{E}_i+kT\ln n_i-kT\ln(N_i-n_i), \qquad (A.7)$$

from which

$$n_i=N_i/\{1+\exp(\mathcal{E}_i-\mu_i)/kT\}, \qquad (A.8)$$

which implies the normal definition of the quasi-Fermi level μ_i. In the above treatment the contribution of the spins has been neglected.

If n_e represents the number of electrons in a continuous parabolic band, it is well known that integration over all energy levels leads, if $N_C=2(2\pi m_ekT/h^2)^{\frac{3}{2}}$ and V is the crystal volume, to

$$F_e=n_e\mathcal{E}_C-n_ekT\ln(VN_C/n_e), \qquad (A.9)$$

and similarly for holes

$$F_h=-p_h\mathcal{E}_V-p_hkT\ln(VN_V/p_h). \qquad (A.10)$$

Differentiating once, we find, if $\mu_e=\partial F/\partial n_e$, $\mu_h=-\partial F/\partial p_h$,

$$n_e=VN_C\exp[(\mu_e-\mathcal{E}_C)/kT], \qquad (A.11)$$

$$p_h=VN_V\exp[(\mathcal{E}_V-\mu_h)/kT], \qquad (A.12)$$

corresponding to Shockley's definition of quasi-Fermi levels for holes and electrons.[33]

The total free energy in a nearly intrinsic semiconductor is found by adding (A.9) and (A.10). Putting $n_e=n_0+\alpha$, $p_h=p_0+\alpha$, and differentiating twice

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[29] H. B. G. Casimir, Revs. Modern Phys. **17**, 343 (1945).

[30] R. E. Burgess, Proc. Phys. Soc. (London) **B68**, 661 (1955).

[31] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1948), Chap. 5.

[32] A. Einstein, Ann. Physik **33**, 1275 (1910).

[33] W. Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand Company, Inc., Princeton, 1950), p. 308.

with respect to α yields

$$f(\text{nearly intr.})=kT(n_0^{-1}+p_0^{-1}). \qquad \text{(A.13)}$$

In the same way for an extrinsic semiconductor, we must add (A.6) and (A.9); putting $n_j=n_0+\alpha$, $n_i=N_i-n_0-\alpha$, and differentiating twice, we find

$$f(\text{extrinsic})=kT\left(\frac{2}{n_0}+\frac{1}{N_i-n_0}\right). \qquad \text{(A.14)}$$

The results (A.13) and (A.14) were used in Sec. 4 to demonstrate that the thermodynamic relaxation time $\tau=R/f$ is in complete agreement with the ordinary statistical expressions.

APPENDIX B. EXTENSION TO DEGENERATE SEMICONDUCTORS

The purpose of this Appendix is to show that the relations which express the spectra in terms of the transition rates [compare (4.7) and (5.7)] retain their validity. The τ's, however, are different and consequently the expressions for the noise in the applied cases like (4.9), (4.13), and (7.9)–(7.11) are different too, if the electron gas in one or both of the bands is degenerate.

To prove the first statement we must rederive Eq. (3.7). Let us first consider the transitions between a degenerate electron gas in the conduction band and localized levels $\mathcal{E}_j$. In a nonequilibrium state the Fermi levels are denoted again by μ_e and μ_j. The method to find the change in the transition rates is the same as that used in Sec. 3; however, we must use a more careful averaging process for the electron gas in the degenerate band, since the transition probabilities for generation and recombination depend on the energy state which the electron occupies in the conduction band. In general, mainly electrons within a distance $2kT$ from the Fermi level will participate in transitions. Under such conditions the net transition rate $\dot{\alpha}_{ej}$ of electrons to the states $\mathcal{E}_j$ has been given by Landsberg and Moss[34]:

$$-\dot{\alpha}_{ej}=\bar{\gamma}_{ej}N_j(1-P_j)n\{1-\exp(\mu_j-\mu_e)/kT\}; \qquad \text{(B.1)}$$

here $\bar{\gamma}_{ej}$ is the transition coefficient, averaged over the states in the conduction band, N_j is as before the number of impurity centers with energy $\mathcal{E}_j$, P_j is the Fermi-Dirac function

$$P_j(\mathcal{E}_j)=\{\exp(\mathcal{E}_j-\mu_j)/kT+1\}^{-1}. \qquad \text{(B.2)}$$

The number of electrons in the conduction band is given by the well-known Fermi integral

$$n=4\pi V(2m_ekT/h^2)^{\frac{3}{2}}\mathfrak{F}_{\frac{1}{2}}\{(\mu_e-\mathcal{E}_C)/kT\}, \qquad \text{(B.3)}$$

where $\mathcal{E}_C$ is the bottom of the conduction band and

$$\mathfrak{F}_k(\eta)=\int_0^\infty x^k dx/[1+\exp(x-\eta)]. \qquad \text{(B.4)}$$

Let us now assume that μ_j and μ_e only slightly depart from the equilibrium value μ_0. Carrying out the variation in (B.1), we see that only the variation of the { } factor gives a contribution:

$$\begin{aligned}-\dot{\alpha}_{ej}&=\bar{\gamma}_{ej}N_j(1-P_{j0})n_0(\mu_e-\mu_j)/kT\\&=p_{ej}{}^0(\mu_e-\mu_j)/kT. \qquad \text{(B.5)}\end{aligned}$$

For the total rate of change $\dot{\alpha}_j$ of the carriers in $\mathcal{E}_j$, we have to add the transition rates with other levels. Equation (B.5) is completely similar to (3.5), and hence the generalized resistances are again given by (3.7).

Secondly we consider the transitions between a degenerate electron distribution in the conduction band and a degenerate hole distribution in the valence band. Since this case is believed to be applicable to indium antimonide, we shall go into slightly more detail. The net generation rate of carriers between the two bands can be expressed as

$$\begin{aligned}-\dot{\alpha}=\int_{\mathcal{E}_C}^\infty\int_{-\infty}^{\mathcal{E}_V} & N_e(\mathcal{E}_e)N_h(\mathcal{E}_h)\\ &\times[P_e(\mathcal{E}_e)(1-P_h(\mathcal{E}_h))\gamma_{eh}(\mathcal{E}_e,\mathcal{E}_h)\\ &-P_h(\mathcal{E}_h)(1-P_e(\mathcal{E}_e))\gamma_{he}(\mathcal{E}_e,\mathcal{E}_h)]d\mathcal{E}_ed\mathcal{E}_h. \qquad \text{(B.6)}\end{aligned}$$

Here the integrand refers to the transitions between the levels $N_e(\mathcal{E}_e)$ in the conduction band and the levels $N_h(\mathcal{E}_h)$ in the valence band; $P_e(\mathcal{E}_e)$ and $P_h(\mathcal{E}_h)$ are the Fermi-Dirac function for the nonsteady state, $\gamma_{eh}(\mathcal{E}_e,\mathcal{E}_h)$ and $\gamma_{he}(\mathcal{E}_e,\mathcal{E}_h)$ are the probabilities per unit time for generation and recombination of hole-electron pairs in $\mathcal{E}_e$ and $\mathcal{E}_h$. Because of the detailed balance between each pair of levels $\mathcal{E}_e$ and $\mathcal{E}_h$ in the equilibrium state [compare (3.4)], the integrand can be transformed to obtain

$$\begin{aligned}-\dot{\alpha}=\int_{\mathcal{E}_C}^\infty\int_{-\infty}^{\mathcal{E}_V} & n(\mathcal{E}_e)p(\mathcal{E}_h)\gamma_{eh}(\mathcal{E}_e,\mathcal{E}_h)\\ &\times\left[1-\exp\left(\frac{\mu_h-\mu_e}{kT}\right)\right]d\mathcal{E}_ed\mathcal{E}_h, \qquad \text{(B.7)}\end{aligned}$$

where $n(\mathcal{E}_e)=N_e(\mathcal{E}_e)P_e(\mathcal{E}_e)$ and $p(\mathcal{E}_h)=N_h(\mathcal{E}_h)\times(1-P_h(\mathcal{E}_h))$. For small $\mu_h-\mu_0$ and $\mu_e-\mu_0$, (B.7) gives

$$-\dot{\alpha}=\tilde{\gamma}_{eh}n_0p_0(\mu_e-\mu_h)/kT=g_0(\mu_e-\mu_h)/kT, \qquad \text{(B.8)}$$

where g_0 is the equilibrium generation rate.

$$\tilde{\gamma}_{eh}=\frac{1}{n_0p_0}\int_{\mathcal{E}_C}^\infty\int_{-\infty}^{\mathcal{E}_V} n(\mathcal{E}_e)p(\mathcal{E}_h)\gamma_{eh}(\mathcal{E}_e,\mathcal{E}_h)\times d\mathcal{E}_ed\mathcal{E}_h. \qquad \text{(B.9)}$$

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[34] P. T. Landsberg and T. S. Moss, Proc. Phys. Soc. (London) **B69**, 661 (1956). Eq. (5). The following changes in notations have been made: $-\dot{\alpha}_{ej}\to\mu_{ej}$, $\mu_j\to F_j$, $\mu_e\to F_l$, $N_j\to G_j$, $\bar{\gamma}_{ej}\to\bar{A}_{ej}$.

The quantity n_0 is given by (B.3) (replacing μ_e by μ_0); obviously a similar expression can be stated for p_0. Equation (B.8) confirms that the expression (4.3) is still valid for transitions between a degenerate electron and hole gas; consequently expression (4.7) applies to the noise. Furthermore, from (B.3) we find that

$$\delta n=\xi_e n_0(\mu_e-\mu_0)/kT,\xi_e=\frac{\mathfrak{F}_{-\frac{1}{2}}((\mu_0-\mathcal{E}_C)/kT)}{2\mathfrak{F}_{\frac{1}{2}}((\mu_0-\mathcal{E}_C)/kT)}.$$

Similarly, for holes

$$\delta p=\delta n=\xi_h p_0(\mu_0-\mu_h)/kT,\xi_h=\frac{\mathfrak{F}_{-\frac{1}{2}}((\mathcal{E}_V-\mu_0)/kT)}{2\mathfrak{F}_{\frac{1}{2}}((\mathcal{E}_V-\mu_0)/kT)}.$$

Thus (B.8) yields

$$-\dot{\alpha}\equiv-\delta\dot{n}=\delta n(1/\xi_e n_0+1/\xi_h p_0)g_0. \qquad \text{(B.10)}$$

Hence,

$$1/\tau=g_0(1/\xi_e n_0+1/\xi_h p_0). \qquad \text{(B.11)}$$

For complete degeneracy of an n-type sample, $\xi_h\approx 1$ and $\xi_e\approx 3kT/[2(\mu_0-\mathcal{E}_C)]$. Then (B.11) is equivalent to a result of MacIntosh and Allen.[35]

Equations (B.11) and (4.7) yield

$$G(f)=\frac{4\xi_e\xi_h n_0 p_0}{\xi_e n_0+\xi_h p_0}\left(\frac{\tau}{1+\omega^2\tau^2}\right). \qquad \text{(B.12)}$$

Integrating the spectrum, the expression for $\langle\Delta n^2\rangle$ is found to be in complete agreement with a recent result of Oliver.[36] For InSb the correction of the ξ's is estimated to be very small (<5%) by these authors.

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Multiple Echoes in Solids

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By the study of the Zeeman resonance of a nucleus having a large quadrupole moment, like iodine, Watkins and Pound have shown that a cubic crystal like KI is never perfect, and that random electrical gradients always exist at the locations of the nuclei. However, by the cw method only a lower and upper limit can be set to the interaction of the quadrupole moment of the nuclei with these gradients. In order to get more information about their distribution, the spin-echo technique, with large rf field, was used. The calculations, performed in the limit of a field much larger that the random quadrupole interaction, show that, if at time $t=0$ we apply a 90° pulse, and at time $t=\tau$ we apply a φ pulse (with an optimum for φ around $\pi/5$), we get: three "allowed" echoes, at times t such that $(t-\tau)/\tau=\frac{1}{2}$, 1 and 2, which are bell-shaped curves; two "forbidden" echoes for $(t-\tau)/\tau=\frac{3}{2}$ and 3, which are derivatives of bell-shaped curves. These predictions are in agreement with the experiment, and from the width of the allowed echoes, an average of the random quadrupole interaction can be determined: this average, expressed in gauss, was found to vary from 18 gauss to 36 gauss in different samples. We could verify, by using this method, that the crushing, as well as the quenching of the crystals increase the magnitude of the random gradients.

IN an ideal cubic crystal of the NaCl type, there should be no electrical gradients at the positions of the nuclei, and therefore the width of the nuclear resonance line should be determined by the magnetic dipole-dipole interaction only. However, Watkins and Pound[1] have shown that in a real cubic crystal, there are always small electrical gradients which, through their interaction with the quadrupole moments of the nuclei, will greatly influence the Zeeman resonance of spins greater than $\frac{1}{2}$. A cw experimental method is not very well suited to study the magnitude of these interactions and, as shall be seen later, only lower and upper limits can be set to them by the study of line shapes. However, since these interactions are static, it is natural to study them by means of spin-echo techniques[2,3] which give more detailed information on their distribution.

I. FORM OF THE INTERACTION

We assume, for simplicity, that the imperfections of the crystal produce electric fields of axial symmetry. The angle θ between the axis of symmetry and magnetic field H, as well as the magnitude of the electrical gradient, vary randomly from one nucleus to the other.

We observe signals of iodine in potassium iodide (or in some cases in sodium iodide), in a magnetic field H of 5000 to 10 000 gauss.

We shall make the calculations in a frame rotating at the Larmor frequency $\omega=\gamma H$ with the z axis along the magnetic field H. The quadrupole interaction for a given nucleus is, in first order,[4]

$$\mathcal{H}_Q=-a\hbar I_z{}^2+\text{constant}, \qquad (1)$$

with

$$a=\tfrac{1}{2}\gamma G(3\cos^2\theta-1). \qquad (2)$$

G is a measure of the strength of the quadrupole

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