Stochastic analysis of multiple-level recombination luminescence and retrapping in the steady state

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A stochastic formulation of the kinetic model for thermally stimulated luminescence, based on van Kampen's Ω expansion, leads to the set of deterministic macroscopic kinetic equations for the model and to a Fokker-Planck equation that governs the various particle number fluctuations. In the weak source limit the expansions for the steady-state macroscopic particle numbers are of fairly simple form, as are those for the eigenvalues of the system of kinetic equations for the expectation values of the fluctuations. Also in this limit, these eigenvalues (which are just the decay constants in the sums of exponential decays that form the recombination radiation correlation functions) separate into three distinct, experimentally distinguishable, sets. These results have been used [Phys. Rev. B **45**, 622 (1992)] to deduce the model parameters for the case of one recombination center and one trapping level; here the analysis is extended to the general case of μ (purely radiative) recombination centers and ν trapping levels whose activation energies are so close that over a suitable temperature range all traps can traffic in electrons with the conduction band. One can still deduce the larger number of model parameters from measurements of the steady-state recombination radiation intensities and their correlation function decay constants at a set of temperatures and electron-hole production rates. It is also shown how to account for nonradiative recombinations and for deep, thermally disconnected traps (which become filled in the steady state).

I. INTRODUCTION

Thermally stimulated luminescence in various materials has been studied theoretically by invoking simplified phenomenological models.[1,2] Not all the parameters of these models can be determined from observations of the recombination radiation that is emitted when a previously irradiated sample is heated.[2,3] Not only are some of the properties of the sample undetermined; one may also question the exact physical meaning of the model parameters as well as the appropriateness of the model itself.

A stochastic formulation of the usual model was developed,[4] and it was shown that in principle it is possible to derive values for all the parameters of a model with one trapping level and one recombination center from a set of observations of the steady-state recombination radiation autocorrelation function at different sample temperatures and with different electron-hole production rates (caused by varying the incident radiation intensity). Here the analysis will be extended to the more realistic model with multiple traps and recombination centers. There is a larger number of parameters to be determined and equations to be solved; extracting values for the model parameters from these solutions becomes more involved.

The analysis will initially assume that the traps are so closely spaced in activation energy that they all contribute appreciably to the electron traffic with the conduction band over a suitable temperature range. All electron-hole recombinations are taken to be radiative (and observable); the presence of nonradiative recombinations will be considered in Appendix A. Since there is more than one recombination center, one can measure not only the radiation autocorrelation function for each center, but also the cross-correlation functions between the recombination emissions from the various centers. The redundancy from such a large number of observations allows one to obtain values for the model parameters from several independent measurements; agreement among the derived values would give confidence that the parameters have physical significance and have been accurately measured.

In the next section steady-state relations for the macroscopic variables of the model, the kinetic equations governing the expectation values of their fluctuations, and an expression for the recombination radiation correlation functions will be quoted; they can be derived by generalizing van Kampen's Ω expansion[4,5] to include multiple traps and recombination centers. Then the weak-source steady-state solutions will be found for the macroscopic variables, as will weak-source expressions for the recombination radiation correlation function (a sum of exponential decays) decay constants. The usefulness of these latter quantities, as functions of temperature and (weak-)source strength, in determining the trap parameters and (with the steady-state intensities) the recombination center parameters will then be shown.

By this stochastic formulation, one can in principle find values for all the parameters of a model with multiple traps and recombination centers. The trap parameters are found by starting from a polynomial with known coefficients (determined from measurements of the decay constants) whose roots are directly related to the trap activation energies. The recombination parameters are then similarly found by starting from a set of coupled nonlinear algebraic equations that involve the (now known) trap parameters, decay constants, and steady-state recombination intensities and whose solutions are the set of probabilities per unit time for a conduction-band electron to recombine with holes in the various centers. All these initial equations must be solved

numerically. The approach is generalized to include the presence of deep, thermally disconnected traps; they become filled in the steady state, which leads to excess holes in the recombination centers. To illustrate this without excessive algebra, only the case of no active electron traps is presented.

II. STOCHASTIC FORMULATION OF THE THERMOLUMINESCENCE MODEL

Consider a material in which, upon electron-hole pair formation due to irradiation, the holes in the valence band can migrate to a set of μ different type recombination centers and the electrons in the conduction band can migrate to a set of ν different type traps (from which they can escape via thermal activation) and to the recombination centers; recombination of these electrons with the holes in the centers produces the thermoluminescence. There is no direct recombination from the traps, only through the conduction band. Recombination is the only loss mechanism for the holes, and every electron-hole recombination results in photon emission; so the luminescence from center i is I_i, the recombination rate in that center. The photons escape from the sample without absorption or other interaction. Nonradiative recombination is addressed in Appendix A, where it is shown how to obtain the I_i from intensity observations. The complicated details of the interaction of the incident radiation with the sample that gives rise to the electron-hole pairs are represented by the parameter J, the number of electrons (holes) produced in a unit volume of the sample conduction (valence) band in a unit time interval. For independent, uncorrelated incident radiation, as is assumed here, this J is a constant macroscopic parameter in the steady state; the master equation for the system probability function will contain additional terms in the presence of correlated incident radiation.[6,7]

The model is illustrated by Fig. 1, and the model parameters and variables are defined in Table I. In the steady state the kinetic equations yield the algebraic relations

$$C_i\phi\psi_i = B_i(M_i-\psi_i)\rho = I_i \quad (i=1,\ldots,\mu), \tag{1}$$

$$\sum_{i=1}^{\mu} C_i\phi\psi_i = \sum_{i=1}^{\mu} B_i(M_i-\psi_i)\rho = \sum_{i=1}^{\mu} I_i = J, \tag{2}$$

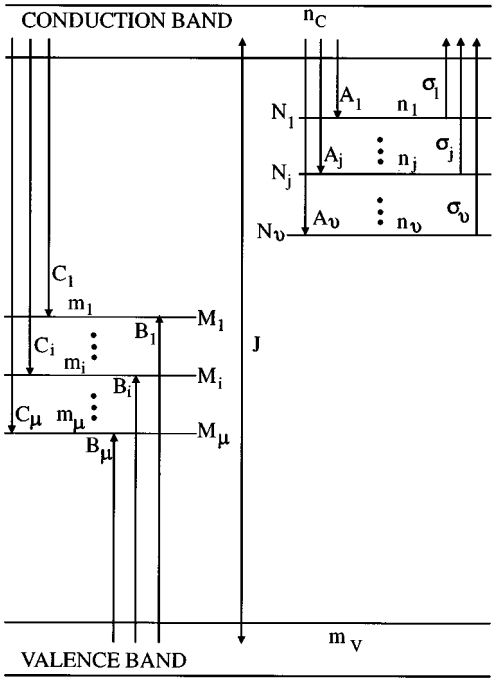

FIG. 1. Energy levels, transition probabilities, and densities for electrons and holes in the conduction and valence bands, multiple trapping states, and multiple recombination centers for a generalized kinetic model that allows electron-hole production during luminescence.

$$\sigma_j\chi_j = A_j(N_j-\chi_j)\phi \quad (j=1,\ldots,\nu), \tag{3}$$

while charge conservation gives

$$\rho+\sum_{i=1}^{\mu}\psi_i = \phi+\sum_{j=1}^{\nu}\chi_j . \tag{4}$$

A generalization of the previous analysis[4] that uses van Kampen's Ω expansion[5] produces the set of kinetic equations, for the expectation values of the fluctuations,

$$\frac{\partial}{\partial t}\langle\tau\rangle = -\sum_{i=1}^{\mu} B_i(M_i-\psi_i)\langle\tau\rangle + \sum_{i=1}^{\mu} B_i\rho\langle\eta_i\rangle, \tag{5}$$

$$\frac{\partial}{\partial t}\langle\xi\rangle = -\left[\sum_{i=1}^{\mu} C_i\psi_i + \sum_{j=1}^{\nu} A_j(N_j-\chi_j)\right]\langle\xi\rangle - \sum_{i=1}^{\mu} C_i\phi\langle\eta_i\rangle + \sum_{j=1}^{\nu}(\sigma_j+A_j\phi)\langle\zeta_j\rangle, \tag{6}$$

$$\frac{\partial}{\partial t}\langle\eta_i\rangle = B_i(M_i-\psi_i)\langle\tau\rangle - C_i\psi_i\langle\xi\rangle - (C_i\phi+B_i\rho)\langle\eta_i\rangle, \tag{7}$$

$$\frac{\partial}{\partial t}\langle\zeta_j\rangle = A_j(N_j-\chi_j)\langle\xi\rangle - (\sigma_j+A_j\phi)\langle\zeta_j\rangle. \tag{8}$$

TABLE I. Identification of model parameters and variables for a sample of volume Ω with $i=1,\ldots,\mu$ recombination centers and $j=1,\ldots,\nu$ traps.

Symbol	Identification
$m_v \rightarrow \Omega\rho+\Omega^{1/2}\tau$	number of holes per unit volume in the valence band
$n_c \rightarrow \Omega\phi+\Omega^{1/2}\xi$	number of electrons per unit volume in the conduction band
$m_i \rightarrow \Omega\psi_i+\Omega^{1/2}\eta_i$	number of holes per unit volume in recombination center i
$n_j \rightarrow \Omega\chi_j+\Omega^{1/2}\zeta_j$	number of electrons per unit volume in trap j
B_i	probability per unit time that a valence-band hole enters center i
C_i	probability per unit time that a conduction-band electron recombines with a hole in center i
A_j	probability per unit time that a conduction-band electron enters trap j
M_i	number of recombination centers i per unit volume
N_j	number of traps j per unit volume
$\sigma_j=s_j\exp(-E_j/k_BT)$	probability per unit time for a trap j electron to escape to the conduction band
s_j	trap j preexponential factor
E_j	trap j activation energy
k_BT	Boltzmann constant$\times$temperature
$H_i \rightarrow \Omega I_i+\Omega^{1/2}h_i$	electron-hole recombination rate/intensity for center i
J	electron-hole production rate per unit volume

Charge conservation yields

$$\langle\tau\rangle+\sum_{i=1}^{\mu}\langle\eta_i\rangle=\langle\xi\rangle+\sum_{j=1}^{\nu}\langle\zeta_j\rangle, \tag{9}$$

from which one can eliminate one of the variables, $\langle\tau\rangle$, for example, from the set (5)–(8). The intensity H_i of recombination radiation from center i is given by the expression

$$\Omega H_i=\Omega I_i+\Omega^{1/2}h_i=\frac{C_i}{\Omega}(\Omega\phi+\Omega^{1/2}\xi)(\Omega\psi_i+\Omega^{1/2}\eta_i), \tag{10}$$

and so $\langle H_i\rangle=I_i$, and in the steady state

$$\begin{aligned}\langle\langle H_i(0)H_k(t)\rangle\rangle&=\langle h_i(0)h_k(t)\rangle\\&=C_iC_k[\phi^2\langle\eta_i(0)\eta_k(t)\rangle+\psi_i\psi_k\langle\xi(0)\xi(t)\rangle\\&\quad+\phi\psi_i\langle\xi(0)\eta_k(t)\rangle+\phi\psi_k\langle\eta_i(0)\xi(t)\rangle].\end{aligned} \tag{11}$$

Since there is more than one intensity, one can measure the cross-correlation as well as the autocorrelation functions for the various intensities. All the equations in this section reduce to the corresponding relations for the single trap and recombination level, $\mu=\nu=1$,[4] and the same approach will be taken in developing their solutions.

III. STEADY-STATE SOLUTIONS

The fluctuations of a system are most readily interpreted when they occur about the steady state, which can be established by exposing the luminescent sample at a fixed temperature to a fixed radiation field that results in a constant electron-hole production rate J and is described by (1)–(4). This production rate will be small for most experimental situations; also in this limit the various steady-state equations have simplified solutions which are more easily inverted to obtain expressions for the model parameters in terms of the observed quantities. In the weak-source limit, the autocorrelation decay constants will separate into three sets with 1, μ, and ν components. Thus expand the macroscopic variables as a power series in J, with the previous subscript notation,[4]

$$\rho=\rho_\alpha J^{\alpha/2}+\rho_{\alpha'}J^{\alpha'/2}+\ldots, \tag{12}$$

$$\phi=\phi_\beta J^{\beta/2}+\phi_{\beta'}J^{\beta'/2}+\ldots, \tag{13}$$

$$\psi_i=\psi_{i\gamma}J^{\gamma/2}+\psi_{i\gamma'}J^{\gamma'/2}+\ldots, \tag{14}$$

$$\chi_j=\chi_{j\delta}J^{\delta/2}+\chi_{j\delta'}J^{\delta'/2}+\cdots. \tag{15}$$

Then (3) requires that $\delta=\beta$ and (2) that $\beta+\gamma=2$ and $\alpha=2$, so that (4) yields $\beta=1$ ($\alpha=2$, $\beta=\gamma=\delta=1$). In obtaining these relations one also finds the lowest-order terms

$$\rho_2=\frac{1}{\Sigma_iB_iM_i}, \tag{16}$$

$$\chi_{j1}=\frac{A_jN_j}{\sigma_j}\phi_1, \tag{17}$$

$$\psi_{i1}=\frac{B_iM_i}{\Sigma_kB_kM_k}\frac{1}{C_i\phi_1}, \tag{18}$$

$$\phi_1=\phi_C\phi_\sigma, \tag{19}$$

where

$$\phi_C\equiv\left(\frac{\Sigma_iB_iM_i/C_i}{\Sigma_kB_kM_k}\right)^{1/2}=\left(\sum_i\frac{I_{i2}}{C_i}\right)^{1/2}, \tag{20}$$

$$\phi_\sigma\equiv\left(1+\sum_j\frac{A_jN_j}{\sigma_j}\right)^{-1/2}. \tag{21}$$

TABLE II. Elements of the determinant for the eigenvalues of the system (6)–(8), with $L_i \equiv C_i\phi + B_i\rho$.

$B_1\rho$	$[B_1\rho+\Sigma_i B_i(M_i-\psi_i)+\lambda]$	$(B_2-B_1)\rho$	$\cdots$	$\cdots$	$(B_\mu-B_1)\rho$	$B_1\rho$	$\cdots$	$\cdots$	$B_1\rho$
$-C_1\psi_1-L_1-\lambda$	$[-B_1(M_1-\psi_1)-L_1-\lambda]$	$L_1+\lambda$	$\cdots$	$\cdots$	$L_1+\lambda$	$-L_1-\lambda$	$\cdots$	$\cdots$	$-L_1-\lambda$
$-C_2\psi_2$	$-B_2(M_2-\psi_2)$	$-L_2-\lambda$	0	0	0	0	0	0	0
$\vdots$	$\vdots$	0	$\ddots$	0	0	0	0	0	0
$\vdots$	$\vdots$	0	0	$\ddots$	0	0	0	0	0
$-C_\mu\psi_\mu$	$-B_\mu(M_\mu-\psi_\mu)$	0	0	0	$-L_\mu-\lambda$	0	0	0	0
$A_1(N_1-\chi_1)$	0	0	0	0	0	$(-\sigma_1-A_1\phi-\lambda)$	0	0	0
$\vdots$	0	0	0	0	0	0	$\ddots$	0	0
$\vdots$	0	0	0	0	0	0	0	$\ddots$	0
$A_\nu(N_\nu-\chi_\nu)$	0	0	0	0	0	0	0	0	$(-\sigma_\nu-A_\nu\phi-\lambda)$

From the next term in the power series, one finds $\alpha'=3$, $\beta'=\gamma'=\delta'=2$. By combining (1) and (2), one obtains the exact steady-state relations

$$\frac{C_i\psi_i}{\Sigma_k C_k\psi_k}=\frac{B_i(M_i-\psi_i)}{\Sigma_k B_k(M_k-\psi_k)}=\frac{I_i}{\Sigma_k I_k}=\frac{I_i}{J}. \tag{22}$$

For the intensity series expansion, one obtains

$$\langle H_i\rangle = I_i = I_{i2}J + I_{i3}J^{3/2}+\cdots, \tag{23}$$

where

$$I_{i2}=\frac{C_i\psi_{i1}}{\Sigma_k C_k\psi_{k1}}=\frac{B_iM_i}{\Sigma_k B_kM_k} \tag{24}$$

and

$$I_{i3}=\frac{I_{i2}}{\phi_1}\left(\sum_k \frac{I_{k2}^2}{C_kM_k}-\frac{I_{i2}}{C_iM_i}\right), \tag{25}$$

which satisfy the conditions $\Sigma_i I_{i2}=1$ and $\Sigma_i I_{i3}=0$. Thus there are each only $\mu-1$ independent I_{i2} and I_{i3}. These conditions are just that in the steady state there are as many electron-hole recombinations per unit time as there are electron-hole pairs created, but the individual recombination rates do not scale linearly with J; thus, the relative distribution of recombinations in the various centers is a function of J.

Upon eliminating $\langle\tau\rangle$ from the set of equations (5)–(8) by the charge conservation condition (9), one has $1+\mu+\nu$ independent equations that can be expressed in matrix form as $d\mathbf{Y}/dt=\mathbf{L}\mathbf{Y}$, where the components of the vector $\mathbf{Y}$ are arranged in the order $\langle\xi\rangle,\langle\eta_1\rangle,\ldots,\langle\eta_\mu\rangle,\langle\zeta_1\rangle,\ldots,\langle\zeta_\nu\rangle$ and the elements of the matrix $\mathbf{L}$ are obtained from (6)–(8); the steady-state values of the macroscopic quantities are used. The solution to this system consists of sums of various exponential decays $\exp(\Lambda_r t)$, where Λ_r are the roots of the characteristic equation $|\mathbf{L}-\lambda\mathbf{I}|=0$, $\mathbf{I}$ being the identity matrix. These eigenvalues are also the decay constants of the recombination radiation correlation functions. One can simplify the determinant $|\mathbf{L}-\lambda\mathbf{I}|$ by performing a series of operations: (i) Add the last ν rows to the first row; (ii) subtract rows 2 through $\mu+1$ from the first row; (iii) add column 2 to the first column and to the last ν columns; (iv) subtract column 2 from column 3 through $\mu+1$. The elements of this modified determinant are displayed in Table II and are exact since no truncated expansions have been introduced yet. In the weak-source limit, only terms in J^0 and $J^{1/2}$ are of interest; when one substitutes the expansions of the macroscopic quantities, truncated to this order in J, the characteristic determinant is simplified since all terms in ρ ($\sim\rho_2 J+\cdots$) will vanish. This latter fact in turn allows one to separate the roots Λ_r into three distinct, experimentally distinguishable, sets. Expand the resulting determinant along the first row (whose only nonvanishing element is in the second column) to obtain

$$\left[\sum_i B_i(M_i-\psi_{i1}J^{1/2})+\lambda\right]D^{\mu\nu}(\lambda)=0, \tag{26}$$

where the elements of the determinant $D^{\mu\nu}(\lambda)$ are given explicitly in Table III; it has nonvanishing terms only along the first row, first column, and diagonal.

In the weak-source limit, the roots $\lambda_r=\lambda_{r0}+\lambda_{r1}J^{1/2}$ of $D^{\mu\nu}(\lambda)$ separate into a set of μ with $\lambda_{r0}=0$ and a set of ν with $\lambda_{r0}\neq 0$. To find the latter values, retain only terms proportional to J^0 upon expanding $D^{\mu\nu}$, so that

$$(\lambda_0)^\mu\begin{vmatrix} 1 & 1 & \cdots & \cdots & 1 \\ A_1N_1 & -\sigma_1-\lambda_0 & & & 0 \\ \vdots & & \ddots & & \\ \vdots & & & \ddots & \\ A_\nu N_\nu & 0 & & & -\sigma_\nu-\lambda_0 \end{vmatrix}=0. \tag{27}$$

Since this determinant is a polynomial in λ_0, one cannot in general obtain explicit expressions for the various roots (and even in the cases where this is possible, the resulting relations are so complicated that it is not feasible to invert them to obtain expressions for the model parameters in terms of the observed quantities λ_0). By setting the expansion of (27) equal to a product of terms linear in the roots

$$\prod_{j=1}^{\nu}(\sigma_j+\lambda_0)+\sum_{j=1}^{\nu}A_jN_j\prod_{k\neq j}(\sigma_k+\lambda_0)\equiv\prod_{r=1}^{\nu}(\lambda_0-\Lambda_{r0})=0, \tag{28}$$

however, one can obtain explicit analytic expressions for specific sums of products of the various roots Λ_{r0}. Equate terms in like powers of λ_0 in (28) to obtain the set of functions

TABLE III. Elements of the determinant $D^{\mu\nu}(\lambda)$ for the eigenvalues of the weak-source limit.

$[-C_1\psi_{11}J^{1/2}-C_1\phi_1J^{1/2}-\lambda]$	$C_1\phi_1J^{1/2}+\lambda$	$\cdots$	$\cdots$	$C_1\phi_1J^{1/2}+\lambda$	$-C_1\phi_1J^{1/2}-\lambda$	$\cdots$	$\cdots$	$-C_1\phi_1J^{1/2}-\lambda$
$-C_2\psi_{21}J^{1/2}$	$-C_2\phi_1J^{1/2}-\lambda$	0	0	0	0	0	0	0
$\vdots$	0	$\ddots$	0	0	0	0	0	0
$\vdots$	0	0	$\ddots$	0	0	0	0	0
$-C_\mu\psi_{\mu1}J^{1/2}$	0	0	0	$-C_\mu\phi_1J^{1/2}-\lambda$	0	0	0	0
$A_1(N_1-\chi_{11}J^{1/2})$	0	0	0	0	$(-\sigma_1-A_1\phi_1J^{1/2}-\lambda)$	0	0	0
$\vdots$	0	0	0	0	0	$\ddots$	0	0
$\vdots$	0	0	0	0	0	0	$\ddots$	0
$A_\nu(N_\nu-\chi_{\nu1}J^{1/2})$	0	0	0	0	0	0	0	$(-\sigma_\nu-A_\nu\phi_1J^{1/2}-\lambda)$

$$F_{01}\equiv-\sum_{r=1}^{\nu}\Lambda_{r0}=\sum_{j=1}^{\nu}(\sigma_j+A_jN_j), \tag{29}$$

$$F_{02}\equiv\sum_{r=1}^{\nu-1}\sum_{s=r+1}^{\nu}\Lambda_{r0}\Lambda_{s0}=\sum_{j=1}^{\nu-1}\sum_{k=j+1}^{\nu}\sigma_j\sigma_k+\sum_{j=1}^{\nu}A_jN_j\sum_{k\neq j}\sigma_k, \tag{30}$$

$$\cdots$$

$$F_{0\nu}\equiv(-1)^\nu\prod_{r=1}^{\nu}\Lambda_{r0}=\left(1+\sum_{j=1}^{\nu}\frac{A_jN_j}{\sigma_j}\right)\prod_{k=1}^{\nu}\sigma_k. \tag{31}$$

The functions F_{0j} are known, since they are found by adding singlets, pairs, triplets, ... of the observed roots Λ_{r0}. If there are ν trapping levels, there are ν of these roots, but each root contains information about all ν traps. Each trap competes against all the other traps for its share of the conduction-band electron traffic, and so the steady-state occupation χ_j and fluctuations thereof, ζ_j, depend on the properties of all traps, not just j. In the lowest order (J^0), this set of eigenvalues does not contain any effect from the recombination centers, even though they also interact with the conduction-band electrons.

To obtain the $J^{1/2}$ coefficients λ_1 for the set of μ eigenvalues with $\lambda_0=0$, set $\lambda=\lambda_1J^{1/2}$ in $D^{\mu\nu}$ and remove all terms in $J^{1/2}$ from the last ν rows of the determinant, which may then be expanded along the first row to yield

$$\prod_{i=1}^{\mu}(\lambda_1+C_i\phi_1)+\left(\sum_{k=1}^{\mu}\frac{B_kM_k}{C_k}\right)^{-1}\phi_1\sum_{i=1}^{\mu}B_iM_i\prod_{s\neq i}(\lambda_1+C_s\phi_1)\equiv\prod_{r=1}^{\mu}(\lambda_1-\Lambda_{r1})=0. \tag{32}$$

This has the same form as (28), and so its roots can be specified by the functions F of (29)–(31) if one makes the identifications $\sigma_j\rightarrow C_i\phi_1$ and $A_jN_j\rightarrow B_iM_i\phi_1(\Sigma_kB_kM_k/C_k)^{-1}$, with the products and sums now running to μ instead of ν. One then has

$$\frac{F_{11}}{\phi_\sigma}\equiv\frac{(-1)}{\phi_\sigma}\sum_{r=1}^{\mu}\Lambda_{r1}=\sum_{i=1}^{\mu}\frac{I_{i2}}{z_i}+\left(\sum_{i=1}^{\mu}z_i\right)^{-1}, \tag{33}$$

$$\frac{F_{12}}{\phi_\sigma^2}\equiv\frac{1}{\phi_\sigma^2}\sum_{r=1}^{\mu-1}\sum_{s=r+1}^{\mu}\Lambda_{r1}\Lambda_{s1}=\sum_{i=1}^{\mu-1}\sum_{k=i+1}^{\mu}\frac{I_{i2}}{z_i}\frac{I_{k2}}{z_k}+\sum_{i=1}^{\mu}I_{i2}\sum_{k\neq i}\frac{I_{k2}}{z_k}\left(\sum_{i=1}^{\mu}z_i\right)^{-1}, \tag{34}$$

$$\cdots$$

$$\frac{F_{1\mu}}{\phi_\sigma^\mu}\equiv\frac{(-1)^\mu}{\phi_\sigma^\mu}\prod_{r=1}^{\mu}\Lambda_{r1}=2\prod_{i=1}^{\mu}\frac{I_{i2}}{z_i}, \tag{35}$$

where

$$z_i\equiv\left(\frac{I_{i2}}{C_i}\right)\frac{1}{\phi_C}, \tag{36}$$

and so $\Sigma_iz_i=\phi_C$. If there are μ recombination centers, there are μ eigenvalues whose lowest dependence $\sim J^{1/2}$. Each such root contains information about all μ recombination centers as well as trapping-level information through the presence of the ϕ_σ. The observed correlation functions (11) are combinations of the solutions for the kinetics of the fluctuation first moments and of the steady-state second moments of the fluctuations. Since both these quantities are derived from the same Fokker-Planck equation, one wants to

ensure that there is no peculiar relationship that would cause the amplitudes of some of the exponential decays to vanish. From the explicit calculations of the $\mu=\nu=1$ case[4] and the symmetry of the Λ_{i1}^{μ} and Λ_{j0}^{ν} in the trap and center parameters, one can argue that just as the single Λ_{11} and Λ_{10} appear in the $J^{1/2}$ terms of the $\mu=\nu=1$ correlation function, so also will the entire sets Λ_{i1}^{μ} and Λ_{j0}^{ν} appear in the $J^{1/2}$ terms of all the general μ,ν correlation functions. This is based on the observation that each decay constant Λ_{i1}^{μ} or Λ_{j0}^{ν} contains in a completely symmetric manner the parameters of all the traps or centers and that in the governing equations only the arbitrary labeling scheme distinguishes one recombination center and its stochastic radiation from any other such center. By similar reasoning, the third type of decay constant, Λ_B of (26), will not appear in the lowest-order J expansion term for any of the general μ,ν correlation functions.

IV. DEDUCTION OF THE MODEL PARAMETERS

In the previous section both the macroscopic and correlation function steady-state values of the model variables were determined for weak electron-hole production in terms of the model parameters. The purpose of this stochastic formulation is to deduce numerical values for these parameters from the various intensity measurements. There are $3\mu+4\nu$ such parameters to be determined, three (C_i,B_i,M_i) for each of the μ recombination centers and four (E_j,s_j,A_j,N_j) for each of the ν trapping levels (although in the lowest order only the product A_jN_j can be determined). The numbers μ and ν are also to be determined, as is J itself in most circumstances. Here one considers the case in which all recombinations are radiative and can be observed and the trapping level activation energies are so close together that they all participate in electron trafficking over the temperature range of the observations. The observed quantities are the μ steady-state recombination radiation intensities $\langle H_i\rangle$ and the $\mu(\mu+1)/2$ independent intensity correlation functions $\langle\langle H_i(0)H_k(t)\rangle\rangle$. By measuring the latter for a set of time delays t, one deduces by standard deconvolution schemes[8–10] the $1+\mu+\nu$ decay constants λ_r. These measurements are performed at a set of electron-hole production rates J for each of a set of temperatures T; this allows one to obtain the J^0 and $J^{1/2}$ terms in the expansions of the various quantities and to separate the λ_r into the three sets Λ_B, Λ_{i1}^{μ}, Λ_{j0}^{ν}, from which one forms the F_{0j} and F_{1i} of (29)–(31) and (33)–(35) that are the $\nu+\mu$ ''observed'' or ''measured'' decay quantities. The μ decay constants associated with the F_{1i} are immediately identified by their $J^{1/2}$ dependence, while the ν decay constants associated with the F_{0j} are identified through their J^0 dependence and strong temperature dependence through the σ. The decay constant Λ_B is specified by the lack of temperature dependence in its J^0 term. One can thus assign the measured decay constants to their appropriate groups and obtain μ and ν as well. To obtain the 3ν trapping parameters, one must measure the νF_{0j} for at least three different temperatures; to obtain the 3μ recombination parameters, one uses the $2(\mu-1)$ independent (J^1 and $J^{3/2}$) terms in the J expansion of the $\mu\langle H_i\rangle$, the μ decay quantities F_{1i} and $\Lambda_{B0},\Lambda_{B1}$.

From (2) and (23) one can obtain J simply by summing the recombination radiation $\langle H_i\rangle$ from all centers i. By considering (23), (26), and similar expressions for Λ^{ν} and Λ^{μ} at two production rates J_1 and J_2, one obtains the J expansion coefficients; of these quantities, only Λ_{B0} and Λ_{j0}^{ν} (and thus the trap parameters) can be obtained solely from relative intensity measurements, i.e., from individually unknown J_1 and J_2 that have a known ratio $\alpha=J_2/J_1$.

In principle, one can use all the information contained in measurements at only three temperatures to obtain the trap parameters; there will be 3ν equations (at three temperatures for each of the νF_{0j}) and 3ν unknowns E_j, s_j, and (A_jN_j). In this approach, first solve the set of ν equations at temperature T_1 to obtain expressions for the $\nu(A_jN_j)$ in terms of the $F_{0j}(T_1)$ and the $\sigma_j(T_1)$; substitution of these expressions into the equations for T_2 and T_3 eliminates the (A_jN_j) and leaves 2ν equations that are nonlinear in the 2ν variables. It does not seem possible to reduce significantly the number of equations and variables by further algebraic manipulation, and so one must solve numerically a set of 2ν nonlinear algebraic equations with coefficients derived from observation to obtain values for the remaining model trap parameters. This is quite difficult in general.

Since the F_{0j} involve only the trapping parameters σ_j $[=s_j\exp(-E_j/k_BT)]$ and A_jN_j, one can try to obtain numerical values for these parameters by manipulating a set of F_{0j} measured at several different temperatures. Equations (29)–(31) are linear in the products A_jN_j, and so if the F_{0j} and σ_j are known at a single temperature, one can immediately obtain values for the A_jN_j. Since (29) is also linear in the σ_j, one approach is to use just F_{01} evaluated at $2\nu+1$ temperatures (with $T_1<T_2<\cdots<T_{2\nu+1}$) such that

$$\left(\frac{1}{k_BT_1}-\frac{1}{k_BT_2}\right)=\left(\frac{1}{k_BT_2}-\frac{1}{k_BT_3}\right)=\cdots=\left(\frac{1}{k_BT_{2\nu}}-\frac{1}{k_BT_{2\nu+1}}\right)\equiv\eta; \quad (37)$$

i.e., the difference between the inverses of adjacent temperatures is constant. The A_jN_j can be eliminated by forming the difference between (29) evaluated at two adjacent temperatures,

$$\Delta F_{l,l-1}\equiv F_{01}(T_l)-F_{01}(T_{l-1})=\sum_{j=1}^{\nu}s_j\exp(-E_j/k_BT_{l-1})[\exp(\eta E_j)-1]. \quad (38)$$

Divide these equations (38) into two groups $(\Delta F_{21},\ldots,\Delta F_{\nu+1,\nu})$ and $(\Delta F_{\nu+2,\nu+1},\ldots,\Delta F_{2\nu+1,2\nu})$; each set can be solved for s_j or s_j $[\exp(\eta E_j)-1]$ in terms of the still unknown quantities $x_j\equiv\exp(\eta E_j)$.

Extensive algebraic manipulation (the major features of which are given in Appendix B) of these equations leads one to a polynomial of the form

$$\prod_{j=1}^{\nu}(x-x_j)=\sum_{j=0}^{\nu}(-1)^jb_jx^{\nu-j}=0, \quad (39)$$

where the coefficients b_j are known from the observed quantities $\Delta F_{l,l-1}$ of (38). Such an equation is readily solved numerically to give the x_j and hence the activation energies E_j,

$$E_j=\frac{1}{\eta}\ln x_j, \tag{40}$$

with η given by (37). Since the E_j are all positive, the observations must be accurate enough to ensure all the roots x_j are greater than unity. One can check these results by also using an F_{1i} evaluated at two temperatures T_1 and T_2, for example,

$$\frac{F_{0\nu}(T_2)}{F_{0\nu}(T_1)}\left[\frac{F_{1i}(T_2)}{F_{1i}(T_1)}\right]^{2/i}=\exp\left(\eta\sum_{j=1}^{\nu}E_j\right)=\prod_{j=1}^{\nu}x_j, \tag{41}$$

to obtain an independent value for the sum of the activation energies. Once the E_j are found, one finds the s_j from the intermediate equations (B1). Finally, the A_jN_j are found from (29)–(31) evaluated at one temperature T_1, for example; this system has solutions ($F_{00}\equiv 1$)

$$A_jN_j=\frac{-(-1)^{\nu}\Sigma_{k=0}^{\nu}(-\sigma_j)^kF_{0,\nu-k}}{\Pi_{k=1,\neq j}^{\nu}(\sigma_j-\sigma_k)}, \tag{42}$$

where the σ and F are evaluated at T_1. From observations at $2\nu+1$ temperatures, analysis of (29) allows one to deduce the trapping parameters E_j, s_j and the products A_jN_j. Most of the information available from the observations is not used, since only F_{01} is considered. An unfavorable consequence of this is that, since a minimum temperature separation is needed to yield an accurate ΔF, in the case of many trapping levels ν the $2\nu+1$ measurements will be spread over a temperature range that may be larger than the region in which all traps partake in electron trafficking [which depends on the function $\exp(-E/k_BT)$].

Since it becomes more difficult to determine the trapping parameters as the number ν of trapping states increases, an alternative approach to these measurements may be useful. Start the set of measurements at a temperature so high that only the deepest trap contains charges in the steady state; the other traps are relatively shallow, and so at this temperature electrons escape so quickly the traps are empty. This temperature must be consistent with the ability to measure the luminescence; for example, it cannot be so high that blackbody radiation from the sample material masks the luminescent radiation. The idea is to make the effective ν, the number of traps partaking in electron trafficking, as small as possible. To be definite, this is taken to be $\nu=1$. The parameters of this trap are then determined by measurements at three temperatures or at two temperatures with both F_{01} and F_{11}. These temperatures are all so high that only the one deepest trap contains electrons. Now lower the temperature into a region in which only a second trap (the second deepest one) also contains electrons. The parameters for this $\nu=2$ system could be found by using the methods discussed earlier in this section; however, it would be much easier to use the already determined $j=\nu$ trapping state parameters to reduce this to a single trap problem for the $j=\nu-1$ trap. Reduce the temperature until a third trap contains electrons and treat this as a single trap $j=\nu-2$ problem since the parameters of the other two traps are already known. Continue this process to determine the trap parameters one trap at a time until they have all been found. If some trapping states are so close together in activation energy that they are always empty or always contain some electrons together, one would use the equation for this effective ν, which is still a great advantage over solving at once for all ν trapping states.

In the general step of this process, suppose that there are $j+1$ trapping states and that the parameters of j of them are known. Then the $j+1$ equations for the $F_{0k}^{(j+1)}$ are not independent. For convenience, consider $F_{01}^{(j+1)}$ and $F_{0,j+1}^{(j+1)}$, which are the sum and product of the $j+1$ trapping state decay constants. They satisfy

$$F_{01}^{(j+1)}(r)-F_{01}^{(j)}(r)=\sigma_{\nu-j}(r)+A_{\nu-j}N_{\nu-j}, \tag{43}$$

$$F_{0,j+1}^{(j+1)}(r)=\sigma_{\nu-j}(r)F_{0,j}^{(j)}(r)+\sigma_{\nu-j+1}(r)\cdots\sigma_{\nu}(r)A_{\nu-j}N_{\nu-j}, \tag{44}$$

where the temperature T_r is denoted by r in the arguments of the functions and all quantities are known except $\sigma_{\nu-j}(r)$ and $A_{\nu-j}N_{\nu-j}$. One immediately finds

$$A_{\nu-j}N_{\nu-j}=\frac{F_{0,j+1}^{(j+1)}(r)-F_{0,j}^{(j)}(r)[F_{01}^{(j+1)}(r)-F_{01}^{(j)}(r)]}{[\sigma_{\nu-j+1}(r)\cdots\sigma_{\nu}(r)]-F_{0,j}^{(j)}(r)}, \tag{45}$$

$$\sigma_{\nu-j}(r)=\frac{-F_{0,j+1}^{(j+1)}(r)+[\sigma_{\nu-j+1}(r)\cdots\sigma_{\nu}(r)][F_{01}^{(j+1)}(r)-F_{01}^{(j)}(r)]}{[\sigma_{\nu-j+1}(r)\cdots\sigma_{\nu}(r)]-F_{0,j}^{(j)}(r)}\equiv R_{\nu-j}(r). \tag{46}$$

Evaluate (46) at temperatures T_1 and T_2 to obtain

$$E_{\nu-j}=\left(\frac{1}{k_BT_1}-\frac{1}{k_BT_2}\right)^{-1}\ln\left[\frac{R_{\nu-j}(2)}{R_{\nu-j}(1)}\right] \tag{47}$$

and

$$s_{\nu-j}=R_{\nu-j}(1)\left[\frac{R_{\nu-j}(2)}{R_{\nu-j}(1)}\right]^{T_2/(T_2-T_1)}. \tag{48}$$

The value of $A_{\nu-j}N_{\nu-j}$ can be obtained from (45) evaluated at T_1.

To find the parameters for the first, deepest, trap, one used measurements at three temperatures. Only two temperatures

each are needed to determine the parameters of the subsequent traps one by one; overall, then, one measures at $2\nu+1$ temperatures, just as in the first method proposed. Similarly, one also does not use all the information F_{0j} available from these measurements; however, the temperatures used here are chosen under the constraint of the distribution of the trap activation energies E_j and not according to the η prescription of (37). Consequently, by combining the methods of determination of the trap parameters all at once or one by one, one can use $2\nu+1$ temperature measurements to obtain the parameters for a fairly arbitrary distribution of trapping state activation energies E_j.

From the previous discussion, it is possible to determine the model parameters of the trapping states solely from the set of recombination intensity correlation decay constants Λ_{j0}^{ν}. One can now turn to the problem of finding the recombination center parameters C_i, B_i, and M_i from the set of intensity correlation decay constants Λ_{1i}^{μ} and Λ_B and the macroscopic recombination intensities I_{i2} and I_{i3}. From (26) one has

$$\Lambda_{B0}=-\sum_{i=1}^{\mu} B_i M_i, \tag{49}$$

$$\Lambda_{B1}=\frac{1}{\phi_1 \Sigma_i B_i M_i}\sum_{k=1}^{\mu}\frac{B_k^2 M_k}{C_k}, \tag{50}$$

so that (24) and (25) yield ($i=1,\ldots,\mu$)

$$B_i M_i=-\Lambda_{B0} I_{i2} \tag{51}$$

and

$$C_i M_i \phi_C=\frac{I_{i2}}{[(\Lambda_{B1}/-\Lambda_{B0})-(I_{i3}/I_{i2})]\phi_\sigma}. \tag{52}$$

Since the quantity ϕ_σ can be found from the Λ^{ν} roots, (33)–(35) are a set of μ nonlinear equations in μ unknown quantities z_i. From (36) one finds

$$C_i=\frac{I_{i2}}{z_i \Sigma_k z_k}. \tag{53}$$

One first solves the μ equations (33)–(35) to obtain the z_i. From (53) one then obtains values for the electron-hole recombination rates C_i, while (52) yields the number of recombination centers,

$$M_i=\frac{z_i}{[(\Lambda_{B1}/-\Lambda_{B0})-(I_{i3}/I_{i2})]\phi_\sigma}. \tag{54}$$

Substitution of these M_i into (51) then yields values for the B_i. Thus one can obtain numerical values for the recombination parameters C_i, B_i, and M_i in a straightforward manner.

Since the factors ϕ_σ and the F_{1i} have the same temperature dependence, the right-hand sides of (33)–(35) are temperature independent; thus, evaluation of these equations at different temperatures will not aid in their solution. For arbitrary μ, one must use numerical methods to obtain values for the z_i from the set of nonlinear equations (33)–(35). The general approach to such a problem is to find initial estimates for the z_i that are as accurate as possible and then to refine these estimates by iterative or other schemes that converge to the correct solution. This can be very difficult to do in several dimensions.[11,12] There may be some assistance in that the (always positive) magnitude of the C_i or z_i will have typical values that arise from the physical properties of the sample material.

From the Λ_{j0}^{ν} one could only obtain the products $A_j N_j$ for the trapping parameters. By also considering the next terms Λ_{j1}^{ν} in the J expansion of these decay constants, one can obtain the A_j by themselves (and thus also the N_j). The Λ_{j1}^{ν} are found from the sum of $1+\mu+\nu$ determinants, which are all the possible ways the determinant for the lowest J^0 order characteristic equation can have only $J^{1/2}$ terms in only one column at a time and J^0 terms in all the other columns. Since the original J^0 characteristic equation vanishes for any of the ν eigenvalues Λ_{j0}^{ν}, any terms or combination of terms that are proportional to it will vanish. One thus obtains, after some algebraic manipulation,

$$\sum_{k=1}^{\nu} A_k \Lambda_{j0}^{\nu} \phi_1 \left[\left(\frac{A_k N_k}{\sigma_k} - 1 \right) \prod_{l\neq k} (\sigma_l+\Lambda_{j0}^{\nu}) + \sum_{l\neq k} A_l N_l \prod_{r\neq k,l} (\sigma_r+\Lambda_{j0}^{\nu}) \right]$$

$$= \Lambda_{j1}^{\nu} \Lambda_{j0}^{\nu} \sum_{k=1}^{\nu} \left[\prod_{l\neq k} (\sigma_l+\Lambda_{j0}^{\nu}) - \sum_{l\neq k} A_l N_l \prod_{r\neq k,l} (\sigma_r+\Lambda_{j0}^{\nu}) \right] + \frac{1}{\phi_1} \prod_{l=1}^{\nu} (\sigma_l+\Lambda_{j0}^{\nu}). \tag{55}$$

Since the $A_j N_j$ are known, this set of ν equations (for $j=1,\ldots,\nu$) linear in the ν unknown quantities A_k is readily solved to yield the A_k (and thus also the N_k) in terms of observable properties of the recombination radiation. One only needs to be able to associate the Λ_{j1}^{ν} with the appropriate Λ_{j0}^{ν} for all ν decay constants.

V. DEEP TRAPS

If the trap activation energies are widely separated, the deep traps will be thermally disconnected from the conduction band for temperatures at which luminescence observations are made. In the steady state these deep traps will be filled and their only effect is an excess number of holes in the

recombination centers and in the valence band; one must be able to fill these deep traps in a reasonable time in order to use the stochastic approach. Previous theoretical investigations have assumed that this deep trap filling is possible,[13,14] as have studies of old samples (such as quartz) in archaeological investigations.[15] Numerical integration of the kinetic equations shows how fast a thermally disconnected trap will fill.[16] In addition, some laboratory results[17,18] show saturation in the thermoluminescent signal, which indicates trap filling or the onset of appreciable radiation damage;[19] however, a sublinear approach to constant thermoluminescent output for increasingly larger dose is not necessarily due to trap saturation in second order processes.[20] There is thus both theoretical and experimental justification for consideration of such filled traps; the purpose of so doing here is to determine the effect of these deep traps on the decay constants of the recombination radiation correlation functions and on the method of deducing the model parameters from them.

Assume the measurements are made over a temperature range so narrow that the shallow traps $j=1,\ldots,g$ all traffic in electrons over this range, while the deeper traps $j=g+1,\ldots,\nu$ are always thermally disconnected and thus filled in the steady state; g is taken to be a definite, fixed number. This system is still described by (1)–(3), (5)–(9), and (11), with the range of (and sums over) j now running only to g, not to ν. The major difference is the charge conservation condition (4), which becomes

$$\rho+\sum_{i=1}^{\mu}\psi_i=\phi+\sum_{j=1}^{g}\chi_j+N, \tag{56}$$

where

$$N\equiv\sum_{j=g+1}^{\nu}N_j \tag{57}$$

is the number of electrons stored in the deep traps and also the number of excess holes in the centers. If one expands the macroscopic variables in the power series (12)–(15), (1)–(3) again yield $\delta=\beta$ and $\beta+\gamma=2$. If the total number of hole sites in the recombination centers is M, where

$$M\equiv\sum_{i=1}^{\mu}M_i, \tag{58}$$

there are two possible cases $N\leqslant M$ and $N>M$. In the first case, all N excess holes will be distributed throughout the recombination centers; in the second case, the centers will all be filled and the $N-M$ remaining excess holes will reside in the valence band. In either case, ψ_i will now have a J^0 term; thus, $\gamma=0$, $\beta=\delta=2$, $\alpha(N<M)=2$, and $\alpha(N>M)=0$. The presence of deep traps gives different exponents because of the additional NJ^0 term in (56). The second term in each expansion (12)–(15) is one power of J higher than the first term, and so $\gamma'=2$, $\beta'=\delta'=4$, α' $(N<M)=4$, and α' $(N>M)=2$. Here only the $N<M$ case will be considered; the same approach can be used in the $N>M$ case.

The intensity expansion (23) becomes

$$\langle H_i\rangle=I_i=I_{i2}J+I_{i4}J^2+\cdots, \tag{59}$$

where

$$I_{i2}=C_i\phi_2\psi_{i0}=B_i(M_i-\psi_{i0})\rho_2 \tag{60}$$

and

$$I_{i4}=C_i(\phi_2\psi_{i2}+\phi_4\psi_{i0})=B_i[(M_i-\psi_{i0})\rho_4-\psi_{i2}\rho_2]. \tag{61}$$

These satisfy the conditions $\Sigma_i I_{i2}=1$ and $\Sigma_i I_{i4}=0$. Similarly, the χ_{j2} are still given by (17), while the lowest-order terms of the other macroscopic quantities are found to be

$$\rho_2=\frac{1}{(M-N)}\sum_i\frac{I_{i2}}{B_i}=\left[\sum_i B_i(M_i-\psi_{i0})\right]^{-1}, \tag{62}$$

$$\phi_2=\frac{1}{N}\sum_i\frac{I_{i2}}{C_i}=\left[\sum_i C_i\psi_{i0}\right]^{-1}, \tag{63}$$

$$\psi_{i0}=\frac{N(I_{i2}/C_i)}{\Sigma_k(I_{k2}/C_k)}, \tag{64}$$

$$\psi_{i2}=\frac{1}{\phi_2}\left\{\frac{I_{i4}}{C_i}-\frac{\psi_{i0}}{N}\left[\sum_k\left(\frac{I_{k4}}{C_k}\right)+\rho_2\phi_2-\phi_2^2\left(1+\sum_{j=1}^{g}\frac{A_jN_j}{\sigma_j}\right)\right]\right\}. \tag{65}$$

Since N has a J^0 dependence, there is thus a different relation between the lowest-order J expansion terms of the macroscopic variables.

The $1+\mu+g$ equations (6)–(8) for the expectation values of the fluctuations from which $\langle\tau\rangle$ has been eliminated by (9) again yield the modified determinant (now only to g, not ν) of Table II. Substitution of the J expansions of the macroscopic quantities into this characteristic equation yields a set of equations (in determinant form) for the terms of the J expansion of the decay constants Λ_r. For $N<M$, in lowest order these roots decouple into three sets as in the absence of filled traps. An immediate consequence of the presence of filled deep traps, and an indication of their presence, is that the series expansions in J for the observed intensities I_i and decay constants Λ_r no longer contain half-integral powers of J. Also, there are now $1+\mu+g$ decay constants, and their distribution according to the lowest power in J (J^0 or J^1) will be modified. (Presumably it would also require a much longer time to set up a steady state when one must first fill some traps; this would be another indication that thermally disconnected traps are present.)

The lowest-order term of the J expansion of the characteristic equation is obtained by using only the J^0 terms of the macroscopic quantities. This leads to

$$(\lambda_0)^{\mu-1}\left[\sum_{i=1}^{\mu}B_i(M_i-\psi_{i0})+\lambda_0\right]D_F(\lambda_0)=0, \tag{66}$$

where $D_F(\lambda_0)$ is the determinant of (27) with the first rows of ones replaced by $[-(\phi_2^{-1}+\lambda_0),-\lambda_0,\ldots,-\lambda_0]$; it defines a polynomial of order $g+1$, and ϕ_2 is also given by (63). The equation $D_F(\lambda_0)=0$ is solved by expanding the polynomial analogous to (28) and equating like powers of λ_0 to yield the set of equations for the F'_{0j} $(j=1,\ldots,g+1)$ for the $g+1$ roots Λ^g_{j0}; these are given in terms of Eqs. (29)–(31) for the F_{0j},

$$F'_{01}\equiv-\sum_{r=1}^{g+1}\Lambda^g_{r0}=\{F_{01}\}+\phi_2^{-1}, \tag{67}$$

$$F'_{02}\equiv\sum_{r=1}^{g}\sum_{s=r+1}^{g+1}\Lambda^g_{r0}\Lambda^g_{s0}=\{F_{02}\}+\phi_2^{-1}\sum_{j=1}^{g}\sigma_j, \tag{68}$$

$$\cdots$$

$$F'_{0g}\equiv(-1)^g\prod_{r=1}^{g+1}\Lambda^g_{r0}\sum_{s=1}^{g+1}\frac{1}{\Lambda^g_{s0}}=\{F_{0g}\}+\phi_2^{-1}\prod_{j=1}^{g}\sigma_j\sum_{k=1}^{g}\frac{1}{\sigma_k}, \tag{69}$$

$$F'_{0,g+1}\equiv(-1)^{g+1}\prod_{r=1}^{g+1}\Lambda^g_{r0}=\phi_2^{-1}\prod_{j=1}^{g}\sigma_j, \tag{70}$$

where the $\{F_{0j}\}$ refer to the expressions on the right-hand side of (29)–(31) with ν replaced by g. This set of equations can be used to obtain the E_j, s_j, (A_jN_j), and ϕ_2^{-1}, which is independent of temperature. Consider F'_{01} evaluated at $2g+1$ temperatures chosen to satisfy (37), and eliminate the A_jN_j and ϕ_2^{-1} by defining $\Delta F'_{l,l-1}=F'_{01}(T_l)-F'_{01}(T_{l-1})$ as in (38). Then use the approach of Appendix B to obtain a polynomial of the form (39), whose roots yield the activation energies E_j. Then the analog of (38) is solved for the s_j, and finally the A_jN_j and ϕ_2^{-1} are found by solving the set of $g+1$ equations (67)–(70) at one particular temperature T_1, for example. One finds

$$\phi_2^{-1}=\frac{F'_{0,g+1}(T_1)}{\Pi_{j=1}^{g}\sigma_j(T_1)}, \tag{71}$$

while (42) again gives the A_jN_j (with ν replaced by g). Thus one can find the trap parameters and ϕ_2^{-1} for $N<M$ (and also for $N>M$) from the set of $g+1$ decay constants Λ^g_{j0}, which are distinguished by their J^0 dependence and by their fairly strong temperature dependence through the σ_j.

To obtain the J^1 coefficients λ_2 for the set of $\mu-1$ eigenvalues with $\lambda_0=0$ of $D_F(\lambda)=0$, keep the J^0 terms in the first two and the last g columns of the determinant of Table II and substitute the J^1 terms in the third through $(\mu+1)^{\text{st}}$ columns of the determinant. If any of the latter columns were to contain J^0 terms, it (and thus the determinant) would vanish for $\lambda_0=0$; this prescription then gives the J^1 terms one seeks. Each of the last g columns contains a single nonzero term σ_j; since these are arranged diagonally, the determinant can be immediately reduced to one with $\mu+1$ rows and columns. The first column terms $(-C_i\psi_{i0})$ of this reduced determinant can be multiplied by $-\phi_2$ to give $+I_{i2}$, and the second column terms $[-B_i(M_i-\psi_{i0})]$ can be multiplied by ρ_2 to give $-I_{i2}$; addition of the second to the first column yields a new column whose only nonzero term is its first one. One then obtains $(L_{i2}\equiv C_i\phi_2+B_i\rho_2)$

$$\begin{vmatrix} I_{12} & (L_{12}+\lambda_2) & \cdots & \cdots & (L_{12}+\lambda_2) \\ I_{22} & (-L_{22}-\lambda_2) & & & 0 \\ \vdots & & \ddots & & \\ \vdots & & & \ddots & \\ I_{\mu 2} & 0 & & & (-L_{\mu 2}-\lambda_2) \end{vmatrix}=0, \tag{72}$$

which yields the polynomial

$$\sum_{i=1}^{\mu}I_{i2}\prod_{k\neq i}(L_{k2}+\lambda_2)\equiv\prod_{r=1}^{\mu-1}(\lambda_2-\Lambda^{\mu}_{r2})=0. \tag{73}$$

By expanding (73) and matching powers of λ_2, one will obtain $\mu-1$ equations for the μ quantities L_{i2} (each of which contains the two unknown parameters C_i and B_i) in terms of the observable intensities I_{i2} and decay constants Λ^{μ}_{i2},

$$F_{21}\equiv-\sum_{r=1}^{\mu-1}\Lambda^{\mu}_{r2}=\sum_{i=1}^{\mu}I_{i2}\sum_{k\neq i}L_{k2}, \tag{74}$$

$$F_{22}\equiv\sum_{r=1}^{\mu-2}\sum_{s=r+1}^{\mu-1}\Lambda^{\mu}_{r2}\Lambda^{\mu}_{s2}=\sum_{i=1}^{\mu}I_{i2}\sum_{k=1,\neq i}^{\mu-1}L_{k2}\sum_{l=k+1,\neq i}^{\mu}L_{l2}, \tag{75}$$

$$\cdots$$

$$F_{2,\mu-1}\equiv(-1)^{\mu-1}\prod_{r=1}^{\mu-1}\Lambda^{\mu}_{r2}=\sum_{i=1}^{\mu}I_{i2}\prod_{k\neq i}L_{k2}. \tag{76}$$

An additional relation involving the L_{i2} will thus be needed to solve this system for the individual L_{i2}.

The J^1 term Λ_{B2} for the decay constant with $\Lambda_{B0}=-\Sigma_iB_i(M_i-\psi_{i0})$ of (66) can be found from the determinant of Table II,

$$\Lambda_{B2}=\sum_{i=1}^{\mu}B_i\psi_{i2}-\frac{1}{-\Lambda_{B0}}\sum_{i=1}^{\mu}B_iI_{i2}. \tag{77}$$

It will also be useful to have expressions for the Λ^g_{j2}, the J^1 terms for the decay constants that start with the Λ^g_{j0} of (67)–(70). The characteristic equation for these eigenvalues can be found by replacing the J^0 terms of the lowest-order characteristic equation with the appropriate J^1 terms one column at a time. In evaluating these determinants, all terms or combination of terms that are proportional to the original lowest-order determinant $D_F(\Lambda^g_{j0})$ will vanish. After some algebraic manipulation, one obtains

$$-\left[\phi_2^{-1}+(-\Lambda_{k0}^g)^2\sum_{j=1}^{g}\frac{A_jN_j}{(\sigma_j+\Lambda_{k0}^g)^2}\right]\Lambda_{k2}^g=\sum_{i=1}^{\mu}C_iI_{i2}+(-\Lambda_{k0}^g)\sum_{i=1}^{\mu}C_i\psi_{i2}+(-\Lambda_{k0}^g)^2\sum_{j=1}^{g}\frac{A_j^2N_j}{(\sigma_j+\Lambda_{k0}^g)}\left[\frac{1}{(\sigma_j+\Lambda_{k0}^g)}+\frac{1}{\sigma_j}\right]. \tag{78}$$

For each of the $g+1$ Λ_{k0}^g, there will be a Λ_{k2}^g. The unknown quantities in (78) will be A_j, $\Sigma_iC_iI_{i2}$, and $\Sigma_iC_i\psi_{i2}$. The simplest case (the only one considered here) is that for which there are no active traps, $g=0$. Physically, there are two ways this can come about. First, if the temperature of the sample is so low that all traps are thermally disconnected from the conduction band, there will be no active traps. The second possibility is to raise the sample temperature so high that all the active traps are so active that any trapped electrons are immediately thermally activated into the conduction band, while the thermally disconnected traps are so deep they are still disconnected and filled in the steady state. In either case, (78) simplifies to the single eigenvalue [$\Lambda_{g2}\equiv\Lambda_{k2}^g(g=0)$ and similarly for Λ_{g0}]

$$\Lambda_{g2}=-\phi_2\left[\sum_{i=1}^{\mu}C_iI_{i2}+(-\Lambda_{g0})\sum_{i=1}^{\mu}C_i\psi_{i2}\right]. \tag{79}$$

From (56), (60)–(63), (66), and (67) with $g=0$ and (29) with $\nu=0$ (so $\Lambda_{g0}=-\phi_2^{-1}$), one obtains

$$I_{i4}=-I_{i2}\sum_k\left(\frac{C_k}{-\Lambda_{g0}}\right)\psi_{k2}+\left(\frac{C_i}{-\Lambda_{g0}}\right)\psi_{i2} \tag{80}$$

$$=I_{i2}\sum_k\left(\frac{B_k}{-\Lambda_{B0}}\right)\psi_{k2}-\left(\frac{B_i}{-\Lambda_{B0}}\right)\psi_{i2}, \tag{81}$$

which along with (65) yields

$$\psi_{i2}=\frac{(I_{i2}/L_{i2})}{\Sigma_l(I_{l2}/L_{l2})}\left(\frac{1}{-\Lambda_{g0}}-\frac{1}{-\Lambda_{B0}}\right). \tag{82}$$

If one momentarily assumes the L_{i2} are all known [from the $\mu-1$ equations (74)–(76) and another as yet unspecified equation], one can find the C_i and B_i in terms of these L_{i2} and the observed quantities. Since $\Sigma_iI_{i4}=0$, (80) or (81) comprises $\mu-1$ independent equations; the additional equation independent of these is given by (79) or (77), and one has μ equations for the μ unknowns C_i [(79) and (80)] or B_i [(77) and (81)]. The ψ_{i2} in all these equations are known by (82), since the L_{i2} are assumed to be known. These two sets have solutions

$$\left(\frac{C_i}{-\Lambda_{g0}}\right)=\frac{L_{i2}\Sigma_r(I_{r2}/L_{r2})}{(\Delta\Lambda_0)}\left[\frac{I_{i4}}{I_{i2}}-\frac{\Lambda_{g2}(\Delta\Lambda_0)+\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k4}L_{k2}}{-\Lambda_{g0}(\Delta\Lambda_0)+\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k2}L_{k2}}\right] \tag{83}$$

and

$$\left(\frac{B_i}{-\Lambda_{B0}}\right)=\frac{L_{i2}\Sigma_r(I_{r2}/L_{r2})}{(\Delta\Lambda_0)}\left[-\frac{I_{i4}}{I_{i2}}+\frac{\Lambda_{B2}(\Delta\Lambda_0)-\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k4}L_{k2}}{-\Lambda_{B0}(\Delta\Lambda_0)-\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k2}L_{k2}}\right] \tag{84}$$

[with $\Delta\Lambda_0\equiv(-\Lambda_{g0})^{-1}-(-\Lambda_{B0})^{-1}$], and so one can obtain the C_i and B_i. If one adds (83) and (84) and eliminates the common factor L_{i2}, one has an additional equation for the L_{i2},

$$1=\frac{1}{(\Delta\Lambda_0)}\sum_r\left(\frac{I_{r2}}{L_{r2}}\right)\left[-\frac{\Lambda_{g2}(\Delta\Lambda_0)+\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k4}L_{k2}}{-\Lambda_{g0}(\Delta\Lambda_0)+\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k2}L_{k2}}+\frac{\Lambda_{B2}(\Delta\Lambda_0)-\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k4}L_{k2}}{-\Lambda_{B0}(\Delta\Lambda_0)-\Sigma_r(I_{r2}/L_{r2})\Sigma_kI_{k2}L_{k2}}\right], \tag{85}$$

which in combination with (74)–(76) provides μ equations for the μ unknown L_{i2}. These equations are nonlinear in the L_{i2} and must be solved numerically. If there are no active traps ($g=0$) and $N<M$, one can thus obtain numerical values for all the model parameters from the observed intensities and correlation decay constants through the analytic relations of this section. The number N of electrons in the thermally disconnected traps (or, equivalently, the number of excess holes in the recombination centers) is then immediately found from (63), while the number of recombination centers is given by (60),

$$M_i=I_{i2}\left(\frac{1}{C_i\phi_2}+\frac{1}{B_i\rho_2}\right). \tag{86}$$

For the more general case ($N<M$) $g\neq0$, the major complication is that the single decay constant Λ_{g0} ($=-\phi_2^{-1}$) now becomes a set of $g+1$ decay constants Λ_{j0}^g, and so determination of the Λ_{j2}^g becomes more involved algebraically, but follows the $g=0$ approach. The decay constants Λ_{B0} and Λ_{B2} are the same, while the single roots Λ_{g0} and Λ_{g2} are replaced by the $g+1$ roots of $D_F(\Lambda_{j0}^g)=0$ and the

$g+1$ associated Λ_{j2}^{g} roots, which can be shown to satisfy (78). The presence of deep traps introduces an additional parameter N; to determine its value, one must observe some additional quantity. For a steady state to exist, the deep traps must be filled; if such filling cannot be done, an alternative approach is to use nonthermal means, such as optical excitation at a wavelength that affects only the deep and not the shallow traps, to stimulate electron trafficking from the deep traps to the conduction band. This is in addition to the steady irradiation and electron-hole production J by ionizing radiation. In such a case, the deep traps will not be filled, but will contain a small, macroscopically constant, number of electrons in the steady state; this is basically the first problem treated here.

VI. CONCLUSION

The application of van Kampen's Ω expansion method to obtain the model parameters for a thermoluminescent material from measurements of the steady-state recombination radiation intensities and their correlation function decay constants has been extended to include multiple trapping levels and recombination centers. The simple case of radiative recombination (so all recombinations are observable) and closely spaced activation energies (so all traps can traffic in electrons over some temperature range) has been considered initially. The larger number of coupled nonlinear equations makes their solution and inversion algebraically more complicated; however, even if one uses only the lowest-order terms in the J expansions, it is still possible to obtain expressions for the model parameters in terms of observed quantities (although at this level the trap parameters A_j and N_j only appear as the products A_jN_j). The main conclusion is that at least in principle one can obtain numerical values for the parameters of the usual thermoluminescence model by observing the statistics of the recombination radiation; the actual determination of these values can be reduced to a smaller set of equations which must be solved numerically. It is also shown that the model parameters can still be obtained in the presence of deep traps and of nonradiative recombinations.

The results of this paper can be summarized and the major aspects highlighted by sketching how one would actually implement this stochastic analysis. One first exposes the sample material at a constant temperature T to a steady radiation source (either ionizing or optical radiation that will produce J electron-hole pairs per second, with J a known quantity if possible) and observes the recombination radiation until all such emissions H_i have stationary mean values $\langle H_i\rangle = I_i$. One then observes the fluctuations h_i around the steady-state intensities; to ensure the system is in the linear noise regime that the approximations of this paper assume, these fluctuations must have a Gaussian distribution (with $\langle h_i\rangle = 0$). These conditions of stationary recombination radiation with Gaussian fluctuations are to be monitored throughout whatever series of measurements one will make. One then measures the intensity correlation functions $\langle\langle H_i(0)H_k(t)\rangle\rangle = \langle h_i(0)h_k(t)\rangle = \Sigma_r Q(i,k,r)\exp(\lambda_r t)$ for a large enough number of times t to allow one to invert these functions to obtain the λ_r. Each such correlation function for the various i,k will lead to the set of decay constants λ_r, and so there can be several independent sets of measurements; in practice, the autocorrelation functions $i=k$ may be easier to obtain. While at the same temperature, repeat the correlation function measurements (at all the times t) for a set of different electron-hole production rates J; then, for a set of different temperatures, repeat the set of J and t measurements. One then has $\lambda_r(J,T)$ for a set of production rates and temperatures. If the J are small, one can obtain the λ_{r0} and λ_{r1} terms for the J expansion of the decay constants as well as the lower order terms I_{i2} and I_{i3} for the expansion of the intensities. Parenthetically, if one measured the recombination radiation during the transient stages of changing J and T, one would have another way to deduce some of the sample material properties.

So far, no theoretical model has been used; one has simply observed the steady-state intensities I_i and their fluctuations, from which one has deduced decay constants λ_r and their J and T dependences. The exact functional form of these dependences indicates which theoretical model is appropriate to use in the analysis; the number of each such λ type will also yield the number ν of traps and μ of recombination centers. Once the proper theoretical model is determined from the data, one can use the analysis presented here to obtain values for the model parameters.

One can modify this stochastic model to include more realistic features that are fairly common. The first is to incorporate the possibility of nonradiative recombinations, as is done in Appendix A, for which one cannot directly observe all the recombinations. The discrete nature of recombination into a particular center causes fluctuations in the number of electrons and holes in the conduction and valence bands, which in turn causes fluctuations in the observable recombination radiation that determines the correlation functions; this observable effect is independent of whether the original recombination is radiative or nonradiative. Since the correlation decay constants can still be measured and since they contain information about all the trap and recombination center parameters, one can still obtain quantitative information in the presence of (and even about the) nonradiative recombinations. The main difficulty is in finding expressions to replace those for the now unobservable I_i and thus to allow a unique solution for the recombination parameters. A second modification is for the trap activation energies to be so widely separated that when the deepest traps are active traffickers the shallow ones will be empty and when the shallow traps are active traffickers the deep ones will be thermally disconnected, i.e., not release any electrons to the conduction band. In the steady state, the deep traps will be filled and their only effect is to produce an inequality in the number of electrons and holes in the bands, recombination centers, and active traps. The power series of the J expansions for the various quantities will be different in this case. Another model modification is the effect of fluctuations in J (due to either intrinsic fluctuations in the radiation source itself or the discrete nature of the interactions between this radiation and the atoms of the sample) on the correlation functions of the recombination radiation. If these source fluctuations are uncorrelated, the original assumption of a deterministic J is still valid. The next step is to show that one can

actually measure the correlation functions and steady-state recombination intensities with enough accuracy to obtain meaningful numerical values for the parameters that describe the sample material. This will involve both experimental technique and numerical analysis of sets of nonlinear equations in the presence of experimental uncertainty.

APPENDIX A: NONRADIATIVE RECOMBINATION

In this stochastic analysis one uses the electron-hole recombination rates I_{i2} and I_{i3} to obtain the recombination center parameters (and the separate A_j and N_j for the traps). For complete radiative recombination, these are just the observed intensities. If nonradiative recombinations occur, as they do in many materials, the observed intensities O_i from the various recombination centers are related to the recombination rates I_i by

$$O_i = \epsilon_i I_i , \tag{A1}$$

where ϵ_i is the radiative efficiency of the recombinations in center i. From (1)–(4) the I_i do not scale linearly with J (although their sum does), and so the observed intensities O_i (J_k) at a series of μ different production rates J_k (not necessarily small) form a set of independent equations

$$\sum_{i=1}^{\mu} I_i(J_k) = \sum_{i=1}^{\mu} \frac{O_i(J_k)}{\epsilon_i} = J_k \quad (k=1,\ldots,\mu). \tag{A2}$$

These can be solved to yield the ϵ_i and thus the I_i by (A1), if one knows the J_k. If one only knows the ratios α_k, $J_k = \alpha_k J$ for some unknown J, one can only determine the relative magnitudes of the ϵ_i. For weak fields, if one can measure the O_{im} for the first μ terms of the J expansion of the O_i, one can solve $\Sigma O_{i2}/\epsilon_i = 1$ and $\Sigma O_{im}/\epsilon_i = 0$ $(m=3,\ldots,\mu+1)$ to obtain the ϵ_i.

For some materials thermal effects are the cause of nonradiative recombination, and one has[21,22]

$$\epsilon_i = \frac{1}{1+G_i \exp(-W_i/k_B T)} . \tag{A3}$$

Observe the recombination radiation at three temperatures that satisfy (37), which will be done anyway to obtain the trap parameters. The I_{i2} are independent of temperature, so one has

$$O_{i2}(T_2) - O_{i2}(T_1) = G_i [O_{i2}(T_1)\exp(-W_i/k_B T_1) - O_{i2}(T_2)\exp(-W_i/k_B T_2)] \tag{A4}$$

and similarly for T_3 and T_2. Then the ratio of these two equations yields the quadratic equation

$$\frac{O_{i2}(T_2) - O_{i2}(T_1)}{O_{i2}(T_3) - O_{i2}(T_2)} = \exp(-\eta W_i)\left[\frac{O_{i2}(T_1)\exp(-\eta W_i) - O_{i2}(T_2)}{O_{i2}(T_2)\exp(-\eta W_i) - O_{i2}(T_3)}\right], \tag{A5}$$

which can be solved for the unknown $\exp(-\eta W_i)$ and thus for the W_i in terms of the observed intensities O_{i2} at different temperatures. The G_i are then found from (A4), and so one has the ϵ_i and thus the I_{i2}, as well as values for the G_i and the W_i of the centers. With the ϵ_i one also finds the I_{i3} from the O_{i3}.

Now suppose some of the recombination centers are totally nonradiative ($\epsilon_i = 0$ for some i). One can still obtain the decay constants Λ_B, Λ_1^{μ}, and Λ_0^{ν} from the radiative centers, and from the Λ_0^{ν} one can still obtain the E_j, s_j, and $A_j N_j$ for the traps. The number of Λ_1^{μ} roots is equal to the total number μ of radiative and nonradiative recombination centers. If the radiative efficiencies ϵ_i are given by (A3) or by some other function of the temperature, intensity observations at a set of temperatures allow one to obtain values for the ϵ_i and the I_i for the radiative centers. If one divides the centers into radiative I_i^{R} $(i=1,\ldots m)$ and totally nonradiative I_i^{NR} $(i=m+1,\ldots,\mu)$, one has

$$\sum_{i=m+1}^{\mu} I_i^{\mathrm{NR}} = J - \sum_{i=1}^{m} I_i^{\mathrm{R}} . \tag{A6}$$

If $m=\mu-1$, there is only one nonradiative center, and one immediately has $I_{\mu 2}^{\mathrm{NR}} = 1 - \Sigma I_{i2}^{\mathrm{R}}$ and $I_{\mu 3}^{\mathrm{NR}} = -\Sigma I_{i3}^{\mathrm{R}}$; in this case, all the recombination rates I_{i2} and I_{i3} are known, and so one can proceed as in the main body of the text to obtain all the model parameters (even for the totally nonradiative center). For $m<\mu-1$, one needs additional relations to find expressions for the individual I_{i2}^{NR} and I_{i3}^{NR} or equivalent relations to substitute for them. With additional algebraic effort one could use higher-order terms in the J expansions of the decay constants λ_r or of the recombination intensities I_i, or one could use the amplitudes of the various exponential decay terms in the intensity correlation functions. The steady-state recombinations and fluctuations thereof of electrons and holes in one center (whether radiative or not) affect the steady state and fluctuations of the conduction-band electrons, the valence-band holes, and the electrons and holes in the other (radiative) centers. Physically, this allows one to determine the nonradiative center parameters solely from optical observations of the steady state and fluctuations of the radiative recombination intensities.

APPENDIX B: INVERSION OF TRAP PARAMETER EQUATIONS

To obtain values for the trap model parameters from (38) evaluated at $2\nu+1$ temperatures arranged according to (37), one solves the two sets of equations

$$\begin{pmatrix} \Delta F_{21} \\ \Delta F_{32} \\ \vdots \\ \Delta F_{\nu+1,\nu} \end{pmatrix} = \begin{pmatrix} 1 & 1 & \cdots & 1 \\ x_1 & x_2 & \cdots & x_\nu \\ \vdots & \vdots & & \vdots \\ x_1^{\nu-1} & x_2^{\nu-1} & \cdots & x_\nu^{\nu-1} \end{pmatrix} \begin{pmatrix} s_1(x_1-1)\exp(-E_1/k_BT_1) \\ s_2(x_2-1)\exp(-E_2/k_BT_1) \\ \vdots \\ s_\nu(x_\nu-1)\exp(-E_\nu/k_BT_1) \end{pmatrix} \tag{B1}$$

and

$$\begin{pmatrix} \Delta F_{\nu+2,\nu+1} \\ \Delta F_{\nu+3,\nu+2} \\ \cdots \\ \Delta F_{2\nu+1,2\nu} \end{pmatrix} = \begin{pmatrix} 1 & 1 & \cdots & 1 \\ x_1 & x_2 & \cdots & x_\nu \\ \vdots & \vdots & & \vdots \\ x_1^{\nu-1} & x_2^{\nu-1} & \cdots & x_\nu^{\nu-1} \end{pmatrix} \begin{pmatrix} s_1(x_1-1)\exp(-E_1/k_BT_{\nu+1}) \\ s_2(x_2-1)\exp(-E_2/k_BT_{\nu+1}) \\ \vdots \\ s_\nu(x_\nu-1)\exp(-E_\nu/k_BT_{\nu+1}) \end{pmatrix}, \tag{B2}$$

where $x_j \equiv \exp(\eta E_j)$. These equations are of the form $\mathbf{\Delta F}_{\rm I} = \mathbf{H}\mathbf{S}_{\rm I}$ and $\mathbf{\Delta F}_{\rm II} = \mathbf{H}\mathbf{S}_{\rm II}$, with $S_{{\rm II}j} = S_{{\rm I}j} x_j^\nu$. Since $\mathbf{H}$ is the same for both sets, $S_{{\rm II}j} - S_{{\rm I}j} x_j^\nu = 0$ can be expressed in determinant form as

$$\begin{vmatrix} (\Delta F_{\nu+2,\nu+1} - \Delta F_{21} x_j^\nu) & 1 & \cdots & 1 & 1 & \cdots & 1 \\ (\Delta F_{\nu+3,\nu+2} - \Delta F_{32} x_j^\nu) & x_1 & \cdots & x_{j-1} & x_{j+1} & \cdots & x_\nu \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ (\Delta F_{2\nu+1,2\nu} - \Delta F_{\nu+1,\nu} x_j^\nu) & x_1^{\nu-1} & \cdots & x_{j-1}^{\nu-1} & x_{j+1}^{\nu-1} & \cdots & x_\nu^{\nu-1} \end{vmatrix} = 0 \tag{B3}$$

for each $j = 1, \ldots, \nu$. An overall factor $(-1)^{j-1}$ that arises in interchanging columns (to place the jth column ΔF in the first column) has been removed. The s_j have now been eliminated, and so only the E_j remain.

To evaluate the determinants (B3), first simplify them by in turn subtracting column $\nu-1$ from column ν, column $\nu-2$ from column $\nu-1$, and so on to end by subtracting column 2 from column 3. Thus the first two columns are unchanged, while the remaining columns have a vanishing first row and all other rows are of the form $x_r^n - x_{r-1}^n$. Now

$$\begin{aligned} x^n - z^n &= (x-z) \sum_{k=0}^{K} [x^k z^k (x^{n-1-2k} + z^{n-1-2k}) - (xz)^{(n-1)/2} \delta_{k,(n-1)/2}] \\ &\equiv (x-z) f_{n-1}(x,z), \end{aligned} \tag{B4}$$

where $K = (n/2) - 1$ (n even) or $K = (n-1)/2$ (n odd). From each of the last $\nu-2$ columns, one then extracts the $\nu-2$ common factors $(x_\nu - x_{\nu-1})$, $(x_{\nu-1} - x_{\nu-2})$, $\ldots, (x_{j+1} - x_{j-1}), \ldots, (x_2 - x_1)$. These columns will now have their second row equal to unity. Subtract adjacent columns as before to replace the 1 by 0 in the last $\nu-3$ columns. Since

$$f_{n-1}(x,y) - f_{n-1}(y,z) = \sum_{k=0}^{n-2} y^k (x^{n-1-k} - z^{n-1-k}) = \sum_{k=0}^{n-2} y^k (x-z) f_{n-2-k}(x,z), \tag{B5}$$

one can again extract the common factors, which now differ by 2 in the subscripts, $(x_\nu - x_{\nu-2})$, $(x_{\nu-1} - x_{\nu-3}), \ldots, (x_{j+1} - x_{j-2}), \ldots, (x_3 - x_1)$. This process is repeated until the determinant is reduced to the form (here $j = 1$ is illustrated)

$$\begin{vmatrix} (\Delta F_{\nu+2,\nu+1} - \Delta F_{21} x_1^\nu) & 1 & 0 & 0 & 0 & \cdots & \cdots \\ (\Delta F_{\nu+3,\nu+2} - \Delta F_{32} x_1^\nu) & x_2 & 1 & 0 & 0 & \cdots & \cdots \\ (\Delta F_{\nu+4,\nu+3} - \Delta F_{43} x_1^\nu) & x_2^2 & (x_2 + x_3) & 1 & 0 & \cdots & \cdots \\ (\Delta F_{\nu+5,\nu+4} - \Delta F_{54} x_1^\nu) & x_2^3 & (x_2^2 + x_3^2 + x_2 x_3) & (x_2 + x_3 + x_4) & 1 & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & & \ddots & \\ \vdots & \vdots & \vdots & \vdots & & & \ddots \end{vmatrix} = 0. \tag{B6}$$

This is expanded to yield

$$\begin{aligned} &(\Delta F_{\nu+2,\nu+1} - \Delta F_{21} x_1^\nu) \prod_{j=2}^{\nu} x_j - (\Delta F_{\nu+3,\nu+2} - \Delta F_{32} x_1^\nu) \prod_{j=2}^{\nu} x_j \sum_{k=2}^{\nu} \frac{1}{x_k} + \cdots \\ &\qquad + (-1)^\nu (\Delta F_{2\nu,2\nu-1} - \Delta F_{\nu,\nu-1} x_1^\nu) \sum_{j=2}^{\nu} x_j - (-1)^\nu (\Delta F_{2\nu+1,2\nu} - \Delta F_{\nu+1,\nu} x_1^\nu) = 0. \end{aligned} \tag{B7}$$

There are ν such equations; call them $B(j)$ for $j=1,\ldots,\nu$. Form the new set of ν equations by taking the differences $B(1)-B(2)$, $B(2)-B(3)$, $\ldots$, $B(\nu-1)-B(\nu)$, $B(\nu)-B(1)$. Each of these equations has an overall factor that may be removed; $\Delta F_{2\nu+1,2\nu}$ is eliminated from all of them. For example, in $B(1)-B(2)$ each term will contain (x_1-x_2). Again, form the differences between these equations after removing these difference factors. The new equations will again each have an overall factor that can be removed, and $\Delta F_{2\nu,2\nu-1}$ will be eliminated. Repeated application of this procedure will eliminate $\Delta F_{2\nu+1,2\nu}$ through $\Delta F_{\nu+3,\nu+2}$ and reduce the original system to one equation

$$\Delta F_{21}\prod_{j=1}^{\nu} x_j-\Delta F_{32}\prod_{j=1}^{\nu} x_j\sum_{k=1}^{\nu} x_k^{-1}+\cdots+(-1)^{\nu+1}\Delta F_{\nu+1,\nu}\sum_{j=1}^{\nu} x_j+(-1)^{\nu+2}\Delta F_{\nu+2,\nu+1}=0. \tag{B8}$$

This equation was obtained by using the $2\nu+1$ temperatures that give the set $(\Delta F_{21},\ldots,\Delta F_{2\nu+1,2\nu})$; one can also use the sets $(\Delta F_{32},\ldots,\Delta F_{2\nu+2,2\nu+1}),\ldots,(\Delta F_{\nu+2,\nu+1},\ldots,\Delta F_{3\nu+1,3\nu})$. Each such set will yield an equation like (B8), the only difference being in the subscripts of the ΔF. One then has a set of ν equations

$$\begin{pmatrix} \Delta F_{21} & -\Delta F_{32} & \cdots & (-1)^{\nu+1}\Delta F_{\nu+1,\nu} \\ \Delta F_{32} & -\Delta F_{43} & \cdots & (-1)^{\nu+1}\Delta F_{\nu+2,\nu+1} \\ \vdots & \vdots & & \vdots \\ \Delta F_{\nu+1,\nu} & -\Delta F_{\nu+2,\nu+1} & \cdots & (-1)^{\nu+1}\Delta F_{2\nu,2\nu-1} \end{pmatrix}\begin{pmatrix} v_\nu \\ v_{\nu-1} \\ \vdots \\ v_1 \end{pmatrix}=-(-1)^{\nu+2}\begin{pmatrix} \Delta F_{\nu+2,\nu+1} \\ \Delta F_{\nu+3,\nu+2} \\ \vdots \\ \Delta F_{2\nu+1,2\nu} \end{pmatrix}, \tag{B9}$$

where v_j is the sum of all j-tuple products of the x_j,

$$v_1=\sum_{j=1}^{\nu} x_j,\quad v_2=\sum_{j=1}^{\nu-1} x_j\sum_{k=j+1}^{\nu} x_k,$$

$$\cdots$$

$$v_{\nu-1}=\prod_{j=1}^{\nu} x_j\sum_{k=1}^{\nu} x_k^{-1},\quad v_\nu=\prod_{j=1}^{\nu} x_j. \tag{B10}$$

One can solve the system (B9), $\mathbf{\Delta F v}=\mathbf{g}$, to obtain expressions for the v_j in terms of known quantities; call these

$$v_j=b_j(\mathbf{\Delta F})=\frac{|\mathbf{\Delta F}_j|}{|\mathbf{\Delta F}|}, \tag{B11}$$

where $|\mathbf{\Delta F}_j|$ is the determinant obtained when the $(\nu+1-j)$th column of $|\mathbf{\Delta F}|$ is replaced by $\mathbf{g}$. One then has the polynomial (with $b_0\equiv 1$)

$$\prod_{j=1}^{\nu}(x-x_j)=\sum_{j=0}^{\nu}(-1)^j b_j x^{\nu-j}=0. \tag{B12}$$

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