culation can appreciably affect the simplicity and even the accuracy of the final result, even though one is dealing with isotropic diffusion.

The use of known values of the self-diffusion correlation factor to help evaluate the $p_1(BB)$ or $B_{b\beta}$ for impurity diffusion is a very useful procedure. This method is especially useful when the structure is composed of interpenetrating sublattices, as in the diamond structure. This approach allowed the present calculation of the correlation factor given in Eqs. (3) and (32) to be at least an order of magnitude more accurate than any previous calculation for the four-frequency-model diamond structure.

The U_q equations used here and in Ref. 1 can also be expressed in matrix form. Expressions for the U_q allow the correlation effects arising from a vacancy at one site in the crystal to be compared with effects from vacancies at other sites, including sites far removed from the impurity. Also, the equations derived here do not require strict mirror symmetry across any plane normal to the diffusion direction, which is important for the present ⟨100⟩ diamond-structure calculation.

[1]J. R. Manning, Phys. Rev. 136, A1758 (1964).
[2]H. Mehrer, Z. Naturforsch. 26, 308 (1971).
[3]H. Bakker, Phys. Status Solidi 38, 167 (1970).
[4]S. M. Hu, Phys. Rev. 177, 1334 (1969).
[5]J. G. Mullen, Phys. Rev. 124, 1723 (1961).
[6]R. E. Howard, Phys. Rev. 144, 650 (1966).
[7]K. Compaan and Y. Haven, Trans. Faraday Soc. 54, 1498 (1958).
[8]J. Bardeen and C. Herring, in *Atom Movements*, edited by J. H. Holloman (American Society for Metals, Cleveland, Ohio, 1951), p. 87; also in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (Wiley, New York, 1952), p. 261.
[9]S. M. Hu (private communication).
[10]J. R. Manning, Phys. Rev. 116, 819 (1959).

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Quantum Efficiency and Radiative Lifetime of the Band-to-Band Recombination in Heavily Doped *n*-Type GaAs

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The dependence of the absolute internal quantum efficiency and the radiative lifetime of the band-to-band recombination on the impurity concentration for melt-grown heavily doped n-type GaAs crystals have been determined from measurements of photoluminescence and optical-absorption spectra, the excess-carrier lifetime, and the external efficiency. It is shown that the observed external efficiency at 2×10^{18} cm^{-3} is determined by the combined effects of the position and slope of the absorption edge, the hole lifetime, the surface loss, and the photon reabsorption of the emitted radiation. The radiative lifetime exhibits a minimum at 1.5×10^{18} cm^{-3} because of the effects of the impurity on the slope and position of the absorption edge. This is in contrast to the case of lightly doped nondegenerate crystals in which the radiative lifetime is inversely proportional to the impurity concentration.

It has been known for some time that the dependence of the externally measured band-to-band recombination efficiency at 300 °K on the impurity concentration in melt-grown n-type GaAs crystals exhibits a maximum at 2×10^{18} cm^{-3}.[1,2] Very little is known, however, about why the maximum should occur at this particular impurity concentration. In this paper, an attempt is made to explain the above observation from a combination of measurements of absolute external efficiency, optical-absorption and photoluminescence spectra, and the excess-carrier lifetime.[3] The absolute internal recombination efficiency and the radiative lifetimes are determined, and it is shown how the surface recombination and photon reabsorption affect the measured external efficiency. It can be said that the concentration dependence of the external efficiency is governed by the surface loss, the position and slope of the absorption edge, and the bulk lifetime of the excess carriers. The efficiency maximum at 2×10^{18} cm^{-3} results from an optimum combination of these factors.

In an optically isotropic medium, the spontaneous emission rate (in photons per unit volume per unit energy) $\gamma_{\text{spon}}(h\nu)$ of the band-to-band recombination at energy $h\nu$ is related to the absorption coefficient $\alpha(h\nu)$ by[4]

$$\gamma_{\text{spon}}(h\nu) = (8\pi N^2/h^3c^2)(h\nu)^2\,\alpha(h\nu)$$

$$\times\left[\exp\left(\frac{h\nu-\Delta E_f}{kT}\right)-1\right]^{-1}, \quad (1)$$

where N is the refractive index, h is Planck's constant, c is the velocity of light, k is Boltzmann's constant, T is the temperature, and $\Delta E_f = E_{fe} - E_{fh}$ is the electron (E_{fe}) and hole (E_{fh}) quasi-Fermi levels, with E_{fe} and E_{fh} measured from the nominal valence-band edge[5] (positive upward). Under weak optical excitation or $(h\nu - \Delta E_f)/kT \gg 1$, $\gamma_{\text{spon}}(h\nu)$ at any point x from the sample surface is given by

$$\gamma_{\text{spon}}(h\nu, x) = (8\pi N^2/h^3c^2)(h\nu)^2\,\alpha(h\nu)e^{-h\nu/kT}\,e^{E_{fe}/kT} \times \Delta p(x)\left[\int_{-\infty}^{\infty}\rho_v(E)\,e^{E/kT}\,dE\right]^{-1}, \quad (2)$$

where $\rho_v(E)$ is the valence-band density of states and $\Delta p(x)$ is the excess-hole concentration at x. The distribution of the excess-hole density $\Delta p(x)$ is determined by the solution of the one-dimensional continuity equation:

$$D\,\frac{\partial^2(\Delta p)}{\partial x^2} + g(x,t) - \frac{\Delta p}{\tau} = \frac{\partial(\Delta p)}{\partial t}, \quad (3)$$

where D is the hole diffusion coefficient, g is the external generation rate, and τ is the excess-hole lifetime. Under constant photoexcitation of the form

$$g = g_0 e^{-\alpha x} = [(1-R)F_0\,\alpha_0/A]\,e^{-\alpha x}$$

(R is the reflectivity, F_0 is the flux density of the excitation light, α_0 is the absorption constant of the excitation light, and A is the excitation beam size) and with a boundary condition at the surface determined by a surface recombination velocity S, the observed photoluminescence spectrum $I(h\nu)$ including the effect of self-absorption is given by[6]

$$I(h\nu) = KA\int_0^{\infty}\gamma_{\text{spon}}(h\nu, x)\,e^{-\alpha x}\,dx$$
$$= KA(8\pi N^2/h^3c^2)(h\nu)^2\,\alpha(h\nu)\,e^{-h\nu/kT}e^{E_{fe}/kT} \times\left[\int_0^{\infty}\rho_v(E)\,e^{E/kT}\,dE\right]^{-1} g_0\tau\,G(h\nu), \quad (4)$$

with

$$G(h\nu) = \frac{S/D + L^{-1} + \alpha_0 + \alpha(h\nu)}{[(S/D)+L^{-1}](\alpha_0 L+1)[\alpha_0+\alpha(h\nu)][\alpha(h\nu)L+1]}, \quad (5)$$

where $L = (D\tau)^{1/2}$ is the hole diffusion length. In Eq. (4), K is a proportionality constant determined by the geometrical arrangement of the detection system and, in the present experiment, is given by[7]

$$K = \frac{4}{(N+1)^2}\left(\frac{\Omega_{\text{det}}}{4\pi}\right)\cos\theta_t, \quad (6)$$

where θ_t is the angle of transmission and Ω_{det} is the solid angle for the detection system. The measured external efficiency can be expressed as

$$\eta_{\text{ex}} = \frac{\int_0^{\infty} I(h\nu)d(h\nu)}{K(1-R)F_0}$$
$$= \frac{8\pi N^2}{h^3c^2}\,e^{E_{fe}/kT}\,\alpha_0\tau\left(\int_{-\infty}^{\infty}\rho_v\,e^{E/kT}dE\right)^{-1} \times\int_0^{\infty}(h\nu)^2\,\alpha(h\nu)e^{-h\nu/kT}\,G(h\nu)\,d(h\nu). \quad (7)$$

The internal efficiency η_{in} can be obtained by setting $G(h\nu) = 1$, which corresponds to no surface recombination ($S = 0$) and no photon reabsorption [$\alpha(h\nu) = 0$]:

$$\eta_{\text{in}} = \eta_{\text{ex}}\,\frac{\int_0^{\infty}(h\nu)^2\alpha(h\nu)e^{-h\nu/kT}d(h\nu)}{\int_0^{\infty}(h\nu)^2\alpha(h\nu)e^{-h\nu/kT}G(h\nu)d(h\nu)}. \quad (8)$$

The radiative lifetime τ_r for a particular process is a quantity defined to describe how efficiently the excess carriers will recombine through that particular process. Mathematically, it is defined from η_{in} as

$$\eta_{\text{in}} = \tau/\tau_r. \quad (9)$$

The internal efficiency η_{in} and the radiative lifetime τ_r can be obtained if we know the parameters η_{ex}, $\alpha(h\nu)$, τ, L, S/D, and α_0. In the present work $\alpha_0 = 4.4\times10^4\ \text{cm}^{-1}$ is taken from Sturge's absorption data extrapolated to 1.96 eV.[8] The quantities L and S/D are obtained by fitting the measured photoluminescence spectrum $I(h\nu)$ to the right-hand side of Eq. (4), which contains the experiments $\alpha(h\nu)$.[6] Thus, by measuring η_{ex}, $I(h\nu)$, $\alpha(h\nu)$, and τ, the values of η_{in} and τ_r can be determined.

The arrangements for optical absorption[6] and photoluminescence[9] have been described elsewhere. The excess-hole lifetime has been measured using the optical phase-shift technique.[10,11] In all cases a He-Ne laser which delivered a power of 1 mW was used as the excitation source. The photoluminescence and excitation powers were measured with a model No. 20A power meter from United Detector Technology. The power meter is capable of measuring power down to 10^{-9} W. The band-to-band luminescence was separated from the excitation light by appropriate filters. All the measurements were carried out at 300 °K. The value for the constant K in Eq. (6) in the present case was found to be 1.12×10^{-3}.

Several Te-doped GaAs crystals prepared by the Bridgman and the Czochralski methods were used in this study. The carrier concentration determined from the reflectivity minimum near the plasma frequency ranges from 2×10^{17} to 6.5×10^{18} cm^{-3}.

The details of determining L and S/D from the combination of photoluminescence and optical-absorption measurements through Eq. (4) were described in a previous paper.[6] The doping dependence of L is replotted here in Fig. 1. These values show good agreement with those reported

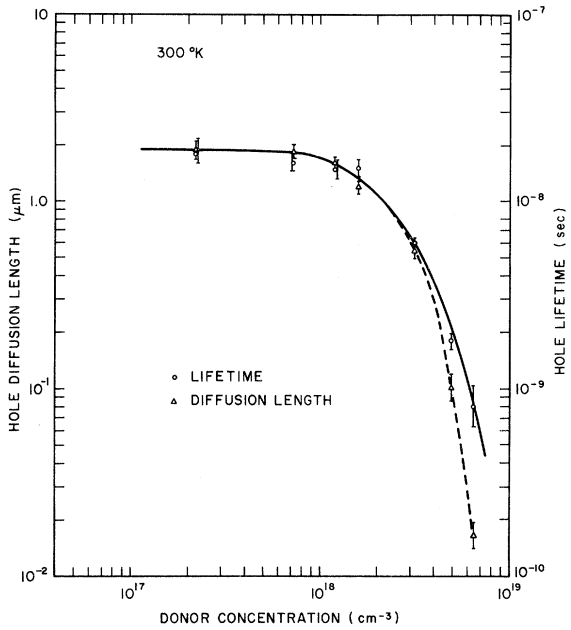

FIG. 1. Dependence of hole lifetime and hole diffusion length on donor concentration.

by others at the same impurity concentration for which the measurements were made.[12] The quantity S/D determined from the above curve-fitting technique is greater than 1×10^5 cm^{-1}. This also agrees with the reported values ranging from 0.5×10^5 to 7.4×10^5 cm^{-1}.[13] The dependence of hole lifetime τ on the impurity concentration n is also plotted in Fig. 1. Both L and τ are nearly independent of n for $n<8\times10^{17}$, indicating that the decay of excess holes is dominated by an identical nonradiative mechanism. The decrease in L and τ for the more heavily doped crystals implies that radiative recombination has become more competitive with nonradiative process. As will be seen (Fig. 3), since the radiative lifetime decreases for $n<8\times10^{17}$ cm^{-3}, reaches a minimum at $n\simeq1.5\times10^{18}$ cm^{-3}, and again increases for $n>3\times10^{18}$ cm^{-3}, we conclude that the onset for the decrease of L and τ at $n=8\times10^{17}$ cm^{-3} is caused by the increase in competition of the radiative recombination rate and that the more rapid decrease in L and τ for $n>3\times10^{18}$ cm^{-3} is due to increasing dominance of other nonradiative recombinations.[11]

The intensity of radiative band-to-band recombination generated inside the crystal will in general not be the same as that measured externally because of reabsorption of the emitted light. The efficiency of this internal band-to-band recombination in turn depends on surface recombination, majority carrier concentration, and other processes. An insight to the solution of these problems can be obtained from determination of internal quantum efficiency, the efficiency affected by the surface alone, and the effect of impurity concentration on these efficiencies. In Fig. 2, we plot the measured external (solid circles) and the deduced internal (open circles) efficiencies as a function of donor concentration. The difference between the two should then be caused by surface recombination and photon reabsorption. The effect of the surface alone can further be obtained by setting $\alpha=0$ in Eq. (5) and substituting the resultant $G(h\nu)$ in Eq. (7), and this result is plotted as open triangles in Fig. 2 for comparison. Note that the recombination efficiency affected only by the surface recombination is less than 10% for all the crystals used in this study. This shows that the use of Eq. (3) for the conservation of minority carriers without making allowance for electron-hole pair generation by the reabsorption is justified.

The surface recombination and photon reabsorption are seen to severely reduce the quantum efficiency that would have been observed externally in the low-doped crystals. This can be understood from the fact that the hole diffusion length is longer than the absorption length in these crystals. About half of the carriers generated within an absorption length will diffuse back to the surface and be lost there. The radiative recombination produced by those which diffuse deep into the crystal and recombine with the majority carriers suffers strong

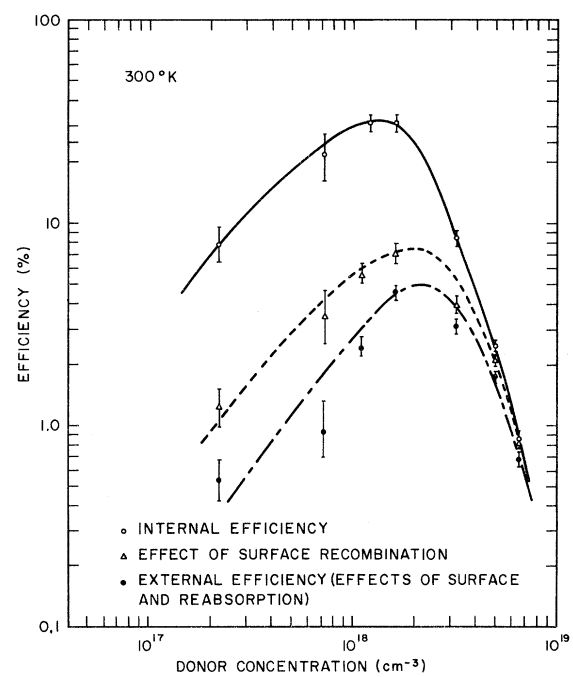

FIG. 2. Internal quantum efficiency, external quantum efficiency, and the efficiency affected only by surface recombination as a function of donor concentration.

reabsorption before it emerges from the crystal. In the extreme case of our crystals ($n \leq 2\times 10^{17}$ cm^{-3}), the external efficiency is only 7% of the internal efficiency.

The internal efficiency increases from 8% at 2×10^{17} cm^{-3} to a maximum of 32% at about 1.5×10^{18} cm^{-3} and then drops rapidly. Other efficiencies follow the same pattern but with maxima shifted to higher doping due to surface and reabsorption effects. It can then be concluded that the maximum of η_{ex} at 2×10^{18} cm^{-3} is a result of combination of the effects of surface and reabsorption, the position of the absorption edge defined here as the photon energy at which $\alpha = 8\times 10^3$ cm^{-1} (a rough measure of the electron Fermi level relative to the valence-band edge[14]), and the bulk lifetime τ. For lightly doped crystals ($n \leq 1\times 10^{18}$ cm^{-3}), the increase in η_{ex} with increasing n is mainly due to the shift of the absorption edge toward the higher-energy side which causes a larger increase of the term $e^{E_{fe}/kT}$ relative to the decrease of the term

$$\int_0^\infty (h\nu)^2 e^{-h\nu/kT}\alpha(h\nu)\,d(h\nu) \quad .$$

For heavily doped crystals, the excess-hole lifetime decreases rapidly. At $n \sim 2\times 10^{18}$ cm^{-3}, the decrease in τ becomes more dominant than the effects of the variation of the position and slope of the absorption edge, or the variation of the term

$$e^{E_{fe}/kT}\int_0^\infty (h\nu)^2\alpha(h\nu)e^{-h\nu/kT}\,d(h\nu) \quad .$$

Therefore η_{in} and η_{ex} start to drop, resulting in a maximum at 2×10^{18} cm^{-3}.

In Fig. 3, τ_r determined from Eq. (9) is plotted as a function of impurity concentration. It shows that a minimum of τ_r can occur in heavily doped crystals as opposed to the monotonically decreasing function of the form for the band-to-band recombination in nondegenerate crystals,[4]

$$\tau_r = 1/\beta n \quad ,$$

where β is the recombination constant connecting states in the conduction- and valence-band edges. In our case, the decrease in τ_r with n for lightly doped crystals is caused by the increase in η_i with n (τ is nearly constant). For more heavily doped crystals ($n \geq 2\times 10^{18}$ cm^{-3}), however, the decrease in η_i is more rapid than τ, and this results in an increase in τ_r with n.

Further insight into the variation of τ_r with the impurity concentration can be obtained. This can be seen from the result of combining Eqs. (7)–(9):

$$\tau_r = (8\pi N^2/h^3c^2)e^{E_{fe}/kT}\alpha_0\left[\int_{-\infty}^{\infty}\rho_v(E)e^{E/kT}\,dE\right]^{-1} \times \int_0^\infty (h\nu)^2 e^{-h\nu/kT}\alpha(h\nu)\,d(h\nu) \quad , \qquad (10)$$

which expresses τ_r in terms of parameters (E_{fe}, ρ_v, and α) related to the intrinsic properties of the crystal. Thus, the radiative lifetime depends only on the particular recombination of interest (band to band in our case) but not on other recombinations, self-absorption, and carrier diffusion. The physical significance underlying the behavior of τ_r with doping can then be interpreted by the combined effects of the position (E_{fe}) and the slope (ρ_v and α below the edge, or the band tails) of the absorption edge as the doping varies. For lightly doped crystals in which the slope of the absorption edge is about the same[14] the decrease in τ_r with n mainly results from the shift of the absorption edge toward higher photon energy. In heavily doped crystals, the slope of the absorption edge is the dominant factor in determining the rise of τ_r with n [the decrease of the term

$$\int_0^\infty (h\nu)^2 e^{-h\nu/kT}\alpha(h\nu)\,d(h\nu) \quad ,$$

with n is faster than the increase of the term $e^{E_{fe}/kT}$ with n]. This interpretation is certainly consistent with what we have explained in terms of the variation of η_i with n, as can be seen from combining Eqs. (7) and (8).

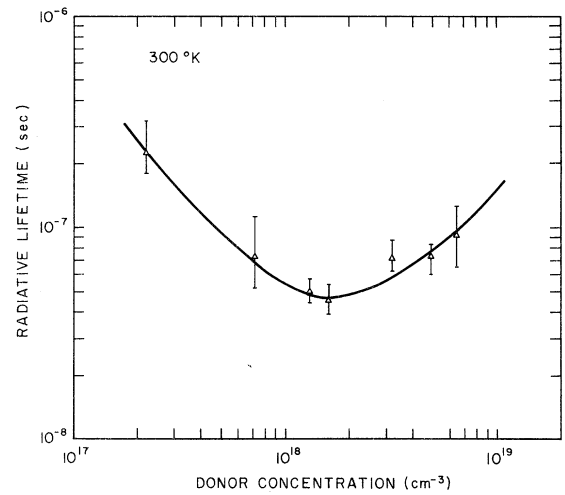

FIG. 3. Dependence of radiative lifetime of the band-to-band recombination on donor concentration.

In conclusion, we have shown that the formation of band tails and the change in the electron Fermi level as a result of impurity doping drastically affect the radiative lifetime of the band-to-band recombination. These effects together with the surface loss and nonradiative trapping or recombination completely determine the dependence of internal quantum efficiency on the impurity concentration. The observed external-effeciency maximum at 2×10^{18} cm^{-3} in n-type GaAs is a direct consequence of this impurity dependence of the internal quantum efficiency and the reabsorption of the recombination radiation.

[1]D. A. Cusano, Solid State Commun. 2, 353 (1964).

[2]C. J. Hwang, J. Appl. Phys. 40, 4591 (1969).

[3]Vilms and Spicer (Ref. 7) have shown that the internal recombination efficiency and radiative lifetime can also be obtained from measurements of external efficiency, optical-absorption spectra, surface photovoltaic effect, and an approximate calculation of the minority carrier mobility. Yu. A. Moma and V. P. Sushkov [Sov. Phys. Semicond. 1, 1278 (1968)] also obtained the same quantities from measurements of minority carrier lifetime, the external efficiency, and a rough allowance for the surface recombination.

[4]G. Lasher and F. Stern, Phys. Rev. 133, A553 (1964).

[5]The band edges of the conduction and valence bands will shift relative to the position of the edges in a pure crystal because of carrier-carrier and carrier-impurity interaction [see, for example, P. A. Wolff, Phys. Rev. 126, 405 (1962)]. The nominal band edges here refer to these shifted edges.

[6]C. J. Hwang, J. Appl. Phys. 40, 3731 (1969).

[7]J. Vilms and W. E. Spicer, J. Appl. Phys. 36, 2815 (1965).

[8]M. D. Sturge, Phys. Rev. 127, 768 (1962).

[9]C. J. Hwang, J. Appl. Phys. 38, 4811 (1967); 39, 1654 (1968).

[10]R. J. Carbone and P. Langaker, Appl. Phys. Letters, 4, 32 (1964); C. J. Hwang, Rev. Sci. Instr. 42, 1084 (1971).

[11]C. J. Hwang, J. Appl. Phys. 42, 4408 (1971).

[12]K. L. Ashley and J. R. Biard, Proc. IEEE Trans. Elec. Devices, ED-14, 429 (1967); D. B. Wittry and D. F. Kyser, J. Appl. Phys. 38, 375 (1967); and L. W. Aukerman, M. F. Miller, and M. McColl, J. Appl. Phys. 38, 685 (1967).

[13]N. M. Kolchanova and D. N. Nasledov, Fiz. Tverd. Tela 8, 1097 (1966) [Sov. Phys. Solid State 8, 876 (1966)]; D. B. Wittry and D. F. Kyser, Proceedings of the International Conference on the Physics of Semiconductors, Kyoto, 1966 (unpublished); J. Phys. Soc. Japan Suppl. 21, 312 (1966).

[14]J. I. Pankove, Phys. Rev. 140, A2059 (1965).

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Dynamics of Electrons and Phonons in Semiconductors

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We present a theoretical study of the evolution of the coupled electron-phonon system in the presence of a strong electric field. A nondegenerate semiconductor of constant carrier density is considered and a numerical solution of the coupled transport equations is performed, the electrons being represented by a Maxwell-Boltzmann distribution with a time-dependent electron temperature $T_e(t)$. It is shown that both $T_e(t)$ and the phonon distribution $N_q(t)$ undergo large deviations even for times of the order of 1 μsec after the application of the electric field. The electron temperature is shown to be generally a nonmonotonic function of time and results are presented for a variety of carrier concentrations and electric field strengths. The calculated phonon distribution generally differs considerably from a Bose-Einstein distribution, so that a phonon temperature cannot be defined.

I. INTRODUCTION

The application of a strong electric field to a semiconductor generally results in significant deviations of both the electron and phonon distributions from their equilibrium values. The phonon deviations are particularly large at low temperatures, where the phonon lifetimes are long,[1-3] being usually determined by boundary scattering.

In such cases one must deal with the coupled electron-phonon system, thus abandoning the usual Bloch assumption of an unperturbed phonon distribution. The effect of phonon heating on the steady-state electrical conductivity has been studied by several authors,[2-4] while it is only recently that studies of the time-dependent case have been undertaken.[5-7] Here one is explicitly interested in the evolution of the electron and phonon distributions when an electric field is applied to the system. This is often of interest experimentally since the electric field pulses employed are often short or of comparable duration to the time necessary to establish the steady state τ_h. The latter is commonly of the order of the phonon transit time L/c, L and c being an approximate sample dimension and sound velocity, respectively, multiplied by a factor η which characterizes the acoustic mismatch between the solid and the heat bath. For the helium-semiconductor contact, $\eta \approx 100$,[4] and the time necessary to reach the steady state is of the order of 10 to 100 μsec.

One of the first analyses of the time-dependent case is that of Paranjape and Paranjape.[5] In their paper an approximate analytic solution was presented, which was based on a simplified treatment of the phonon distribution, where several time-de-