Green's-function formalism of electronic states in heavily doped semiconductors and its application to a problem of inter-valence-band absorption

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A semiempirical method is presented for calculating the electronic states in heavily doped semiconductors in terms of the one-electron Green's function. It has been shown previously that the theory developed on the basis of the semiempirical pseudopotential approach gives a satisfactory description of the impurity-band tail relevant to the heavy-mass band. On the other hand, it is shown in this paper that the theory gives a poor description of the impurity- and phonon-scattering effect on the intraband states even if the theory also takes into account the phonon scattering. Therefore the theory is improved in such a way as to take special account of the intraband states. The new theory is tested by calculating the inter-valence-band absorption constant with the use of this theory and by comparing the theoretical results with experiments. It is shown that the new theory gives a satisfactory description of the electronic states at all energies.

I. INTRODUCTION

Description of the electronic states in terms of the Green's function is a powerful tool for analyzing both optical and electrical properties of heavily doped semiconductors. There are two factors affecting these properties. One is the impurity-band tail, which appears as a result of the heavy doping and affects various physical processes. The other is the impurity and phonon scattering, which enhance physical processes such as inter-valence-band absorption,[1] free-carrier absorption,[2] and Auger recombination.[3–5] In practical cases the above two factors are especially important in the heavy-hole band owing to the large effective density of states.

Previously, the present author has developed the semiempirical pseudopotential (ps) approach[6] to the Green's-function formalism of the electronic states in heavily doped semiconductors. This approach has resulted in a satisfactory description of the impurity-band tail relevant to the heavy-hole band, while all other previous approaches have been found to give poor descriptions. Unfortunately, however, it is shown later that the ps approach gives a poor description of the impurity- and phonon-scattering effect on the intraband states, even when the ps approach is modified to include the phonon-scattering effect also.

This paper presents an improved method of coherently discussing both the band tail and the intraband states under the influence of the impurity and phonon scattering, starting from the ps theory. The theory is tested by calculating the inter-valence-band absorption constant, which is sensitive to the scattering process.

This paper is organized as follows. In Sec. II a discussion of the ps approach is given. In Sec. III an improved theory is given and then theory and experiments are compared.

II. DISCUSSION OF THE ps APPROACH

For the impurity-scattering problem, we use the one-electron Green's function $G^R(l,\mathbf{k};\omega)$, which is obtained by taking an ensemble average of the two-wave Green's function over the impurity sites; here l is the band index, $\mathbf{k}$ the wave vector, and ω the energy parameter. Assuming singly ionized hydrogenic impurities of one species, the previously developed ps approach gives

$$G^R(l,\mathbf{k};\omega)=\frac{\epsilon_0}{|Z|e^2\lambda}\bar{G}^R(\Omega)\,, \tag{2.1}$$

$$\bar{G}^R(\Omega)=\frac{1}{i}\int_0^\infty d\xi\exp[i\xi\Omega+\gamma g(\xi)]\,, \tag{2.2}$$

$$g(\xi)=\int_0^\infty dx\,x^2\{\exp[-i\xi h^{\rm ps}(x)]+i\xi h(x)-1\}\,, \tag{2.3}$$

$$\Omega=\frac{\epsilon_0}{|Z|e^2\lambda}[\omega-E_l(\mathbf{k})]\,, \tag{2.4}$$

$$h(x)=\frac{Z}{|Z|}\frac{1}{x}\exp(-x)\,, \tag{2.5}$$

$$\gamma=\frac{4\pi n_i}{\lambda^3}\,, \tag{2.6}$$

where e is the electronic charge, ϵ_0 the static dielectric constant of the host lattice, λ the free-carrier inverse screening length calculated self-consistently from the Green's function,[6] Z the sign of the carrier charge times the valency of the impurity with respect to the host lattice, n_i the impurity concentration, and $E_l(\mathbf{k})$ the band energy given as $E_l(\mathbf{k})=\hbar^2k^2/(2m_l)$, where m_l is the effective mass for the band l and $\hbar$ is Planck's constant divided by 2π. $E_l(\mathbf{k})$ and ω are measured from the band edge into the band as the positive direction. $h(x)$ is the potential due to an impurity, given in normalized units. $h^{\rm ps}(x)$ is the pseudopotential in question, which is given as $h^{\rm ps}(x)=h(x)+h^r(x)$. Especially when $h^r(x)=0$, Eqs. (2.1)–(2.6) reduce to an expression first obtained by Bonch-Bruevich[7] and derived by the present author[4] in a different approach. Let us call these approaches the Bonch-Bruevich–Takeshima (BT) approach hereafter. It has been shown[6,8] that the BT approach gives a poor description of the impurity-band tail relevant to the

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heavy-hole band, although this approach may be useful[6] for describing the impurity scattering in the conduction band.

In $h^{ps}(x)$, $h^r(x)$ is an essential part of the ps approach and takes a complex form not shown here. On one hand, the BT approach with $h^{ps}(x)=h(x)$ is the case in the classical limit where a sufficiently slowly varying potential is assumed. On the other hand, $h^r(x)$ in the ps approach offers a quantum correction, representing a rapidly varying part of the impurity potential. Note that $h^r(x)$ depends on ω and should be zero at high energies, i.e., $\omega \gg 0$. Nevertheless, $h^r(x)$ has no clear cutoff beyond which $h^r(x)$ rapidly tends to zero. This means that $h^r(x)$ is not adequate for the description of the intraband states.

In the following we test the ps approach by discussing the inter-valence-band absorption in terms of this approach. In Fig. 1 are shown the two kinds of inter-valence-band transitions that we consider hereafter, i.e., the transition from the spin-split-off band (SB) to the heavy-hole band (HB) and that from the light-hold band (LB) to the HB. Let us call these transitions the SH absorption and the LH absorption, respectively. The SH absorption is known[1] to be strongly enhanced by some scattering which relaxes the momentum-conservation requirement in the transition. Since the scattering effect is efficient in a heavy-mass band,[3] we consider the effect on the HB but neglect that on the SB and LB. Neglecting the hole population in the LB and SB under a sufficiently large photon energy, we obtain the absorption constant $\alpha(\omega_{ph})$ for a photon energy ω_{ph} as[1]

$$\alpha(\omega_{ph})=-\frac{2e^2\hbar}{\pi^2 c m_0(\epsilon_\infty)^{1/2}}\int_0^\infty dk\, k^2 f_{12}(\mathbf{k})(1-\theta_1) \times \mathrm{Im}G^R(l_1,\mathbf{k};\omega_1)\,, \quad (2.7)$$

where c and m_0 are the light velocity and the electron mass, both *in vacuo*, ϵ_∞ is the high-frequency dielectric constant, and f_{12} is the oscillator strength between the states $(l_1,\mathbf{k})$ and $(l_2,\mathbf{k})$; here l_i denotes the band i with $i=1$ referring to the HB and $i=2$ to the LB or SB. θ_1 is the Fermi-Dirac distribution function at an energy ω_1. The energy-conservation requirement reads $\omega_1 = E_2(\mathbf{k})-\omega_{ph}$, where $E_2(\mathbf{k})$ is the energy for band 2 measured from the valence-band edge into the band as the positive direction. Finally, $G^R(l_1,\mathbf{k};\omega_1)$ is the retarded Green's function for band 1, i.e., the HB, whose discussion is the central problem.

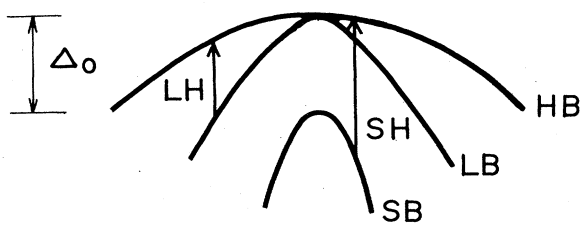

FIG. 1. IVBA due to SH and LH transitions, where impurity effects are not shown.

Hereafter, the calculation is done on p-type GaAs. For the calculation of the inter-valence-band absorption (IVBA), we take into account the anisotropy of the valence bands as described in Ref. 9. As for the band-tail calculation we take the effective—density-of-states mass to be $0.45m_0$. The energy dependences of the effective masses and the oscillator strengths relevant to the LB and SB are calculated by the $\mathbf{k}\cdot\mathbf{p}$ perturbation method[10] or obtained from the realistic band picture of Chelikowsky and Cohen[11] and from Ref. 12. For instance, we use the heavy-hole masses $0.64m_0$, $0.70m_0$, and $0.35m_0$ in the $\langle 110\rangle$, $\langle 111\rangle$, and $\langle 100\rangle$ directions, respectively, and the SB masses $0.079m_0$, $0.10m_0$, and $0.10m_0$ in the same respective directions.

Let us define the IVBA cross section σ through $\alpha=\sigma p$, where p is the hole concentration. Let us assume p to be equal to the acceptor concentration n_A unless stated otherwise. Figure 2 illustrates σ's at 300 K, which are calculated from the ps approach for various values of n_A, with solid lines. In the calculation, this approach has been modified to include the phonon-scattering effect,[6] details of which are described later. It should be noted that the SH absorption occurs in a range of $\omega_{ph}>\Delta_0$ where Δ_0 is the spin-split-off energy. It is seen that the σ curve approaches a certain curve with a decreasing value of n_A. This is a result of the fact that the impurity effect becomes insignificant at small values of n_A. In fact, the band tail almost disappears at $n_A \lesssim 10^{18}$ cm^{-3}, as is seen in Fig. 3, where the band tails calculated from the ps approach are shown for various values of n_A; here the phonon effect has also been incorporated.

On the other hand, Fig. 4 illustrates the cross section of the phonon-assisted IVBA at 300 K with a dashed line. Here, only the phonon-scattering effect has been considered, and no account has been taken of the band tail. The cross section in this approach is almost independent of n_A under $n_A \lesssim 10^{19}$ cm^{-3}. Figure 4 also illustrates the same curve as that given in Fig. 2 for $n_A=10^{18}$ cm^{-3}

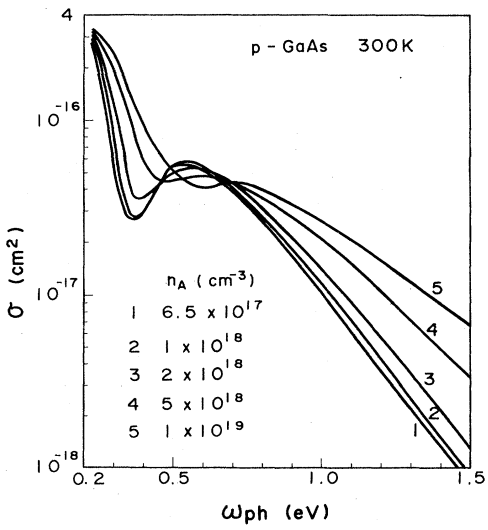

FIG. 2. σ vs ω_{ph}, with n_A as a parameter, calculated in the ps approach for p-type GaAs at 300 K.

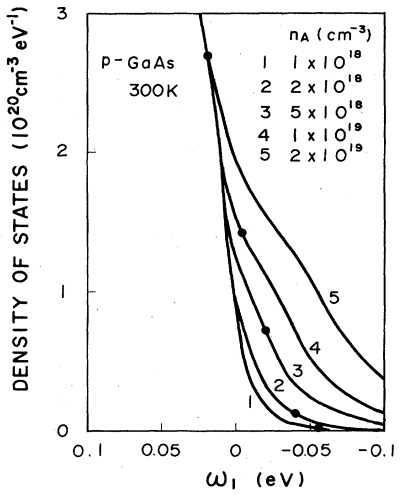

FIG. 3. Density of states versus energy ω_i, with n_A as a parameter, calculated in the ps approach for p-type GaAs at 300 K. A dot attached to each curve shows the Fermi level.

with a dotted-dashed line: A solid line in Fig. 4 is referred to in Sec. III. It is seen that the ps approach (a dotted-dashed line) and the phonon-effect approach (a dashed line) give results very different from one another, although both results should almost agree at such a small value of n_A. Note that the pure IVBA cross section, though not shown here, lies far below the dotted-dashed line. In view of this fact and the above difference, the phonon effect is not considered to be incorporated into the ps approach in a proper way. A high-energy range of photons corresponds to a high-ω_1 range, so that the inadequacy of the theory is ascribed mainly to that of using $h^r(x)$ in a high-ω_1 range. Therefore an improved theory is given in Sec. III.

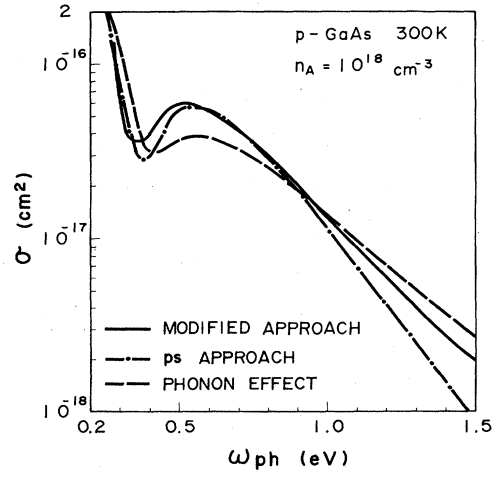

FIG. 4. σ's calculated as functions of ω_{ph} in the modified approach (——), the ps approach (—·—), and the phonon-effect approach (——) for p-type GaAs with $n_A=10^{18}$ cm^{-3} at 300 K.

III. IMPROVED THEORY

Although $h^r(x)$ should vanish at high ω's, $h^r(x)$ can be infinite at a value of x relevant to a given ω. This situation comes from the fact that $h^{ps}(x)=h(x)+h^r(x)$ is obtained by retaining the first two terms in a series expansion of an operator. Actually, inclusion of all the terms is necessary though not practical. Instead, we should rather take $h^r(x)=0$ at high ω's. This is just the BT approach. However, it has been shown[6] that the BT approach is not useful for a heavy-mass band. As an alternative method, we make use of the fact that the impurity-scattering effect is small at high energies. Then we can use the single-site Born approximation. In this approximation the assumption of the slowly varying impurity potential is not necessary, in contrast to the BT approach. Using the second-order Born approximation[1,13] and taking into account the phonon-scattering effect up to first order in the electron-phonon interaction,[3] we obtain

$$G^R(l,\mathbf{k};\omega)=\frac{1}{\omega-E_l(\mathbf{k})-\Sigma^R(l,\mathbf{k};\omega)}\ , \tag{3.1}$$

where the self-energy $\Sigma^R(l,\mathbf{k};\omega)$ is given by

$$\mathrm{Im}\Sigma^R(l,\mathbf{k};\omega)=-\frac{2m_l}{\hbar^2}[AH_1(k,k_0)+BH_2(k,k_0)+CH_3(k,k_0)]\ , \tag{32}$$

neglecting the real part of the self-energy. Here we define

$$H_1(k,k_0)=2k_0-\frac{\lambda^2}{k}\left[\ln\left|\frac{(k+k_0)^2+\lambda^2}{(k-k_0)^2+\lambda^2}\right|-\tfrac{1}{2}\lambda^2H_3(k,k_0)\right]\ , \tag{3.3}$$

$$H_2(k,k_0)=\frac{1}{2}\left[\ln\left|\frac{(k+k_0)^2+\lambda^2}{(k-k_0)^2+\lambda^2}\right|-\lambda^2H_3(k,k_0)\right]\ , \tag{3.4}$$

$$H_3(k,k_0)=\frac{1}{(k-k_0)^2+\lambda^2}-\frac{1}{(k+k_0)^2+\lambda^2}\ , \tag{3.5}$$

$$k_0=\left[\frac{2m_l}{\hbar^2}\omega\right]^{1/2}\ , \tag{3.6}$$

$$A=\frac{1}{8\pi}\left[\frac{1}{c_l}\Xi^2T+\frac{1}{2\bar{c}}E_{npo}^2[1+2P(\omega_{op})]\right]\ , \tag{3.7}$$

$$B=\frac{1}{8\pi}\left[e^2P_{pe}^2T+\frac{2\pi e^2}{\epsilon^*}[1+2P(\omega_{op})]\right]\ , \tag{3.8}$$

$$C=\frac{n_i}{16\pi}\left[\frac{4\pi e^2}{\epsilon_0}\right]^2\ , \tag{3.9}$$

where Ξ is the acoustic deformation potential, E_{npo} the nonpolar-optical deformation potential, P_{pe} the piezoelectric constant, $(\epsilon^*)^{-1}=\epsilon_\infty^{-1}-\epsilon_0^{-1}$, c_l the longitudinal spherical average elastic constant, $\bar{c}$ the averaged elastic constant, ω_{op} the longitudinal-optical—phonon energy, T the thermal energy, and $P(\omega_{op})$ the Bose-Einstein distri-

bution function. The first and second terms in square brackets in Eq. (3.2) represent the phonon scattering, and the third term represents the impurity scattering. The values of the above parameters used for the calculation on GaAs are found in Ref. 3.

Let us use Eqs. (3.1)—(3.9) for the intraband range, i.e., $\omega_1 > 0$, and Eqs. (2.1)—(2.6) for the band-tail range, i.e., $\omega_1 < 0$. However, we use Eqs. (2.1)—(2.6), i.e., the ps approach, in calculating the energy density of states and the free-carrier screening length for convenience, since the scattering may have no serious effect on those quantities in the intraband range. The Fermi levels calculated in this way are shown in Fig. 3 with a dot on each curve.

The IVBA cross section calculated from the modified approach above is shown for $n_A = 10^{18}$ cm^{-3} at 300 K with a solid line in Fig. 4. It is seen that a result of the modified approach is nearer to that of the phonon-effect approach (a dashed line) than that of the ps approach (a dotted-dashed line), while the line of the modified approach nearly agrees with that of the ps approach at low energies. Slightly smaller values of σ at high energies for the modified approach than for the phonon-effect approach are mainly due to the fact that the Fermi level is pulled down by the band tail in the modified approach.

Figure 5 illustrates the IVBA cross sections for various values of n_A $(=p)$. The cross section is almost independent of n_A in a range of $n_A \lesssim 2\times10^{18}$ cm^{-3} as a result of the fact that the phonon-scattering effect predominates over the impurity-scattering effect and that the band-tail effect is insignificant. On the other hand, the cross section depends on n_A in a range of $n_A > 2\times10^{18}$ cm^{-3}.

When p is varied but n_A is fixed at a value, as is the case of the carrier injection, the absorption cross section is only weakly dependent on p. This means that α depends on p through the relation $\alpha = \sigma p$, but that σ depends on only n_A.

Now comparison between the modified calculation and experiments is done on p-type GaAs at 300 K. In Fig. 6 a solid line shows a theoretical result for n_A $(=p) \leq 2\times10^{18}$ cm^{-3}, and a dashed line[14] and a dotted line[15] show experimental results for n_A $(=p) = 6.8\times10^{17}$ and 10^{18} cm^{-3}, respectively. It is seen that the theory and the experiments agree well in a range of high photon energy. In a low-energy range, however, agreement is not so good. This may be partly because we have not considered the transition from the SB to the LB, and partly because the LH absorption is very sensitive to the LB structure, which we know only roughly. However, agreement between the phonon-effect approach and the experiments is much worse in the low-energy range.

Let us test the modified approach at a higher photon energy, in which there is no direct observation of the ab-

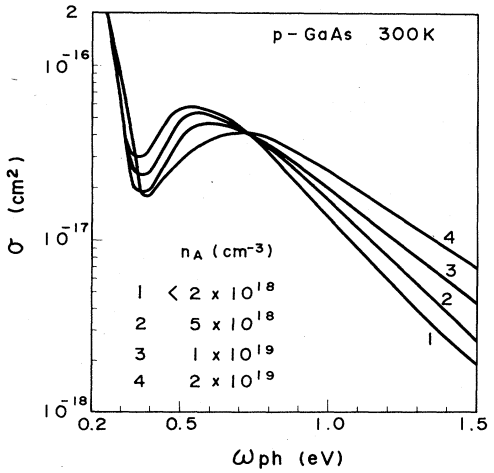

FIG. 5. σ vs ω_{ph}, with n_A as a parameter, calculated in the modified approach for p-type GaAs at 300 K.

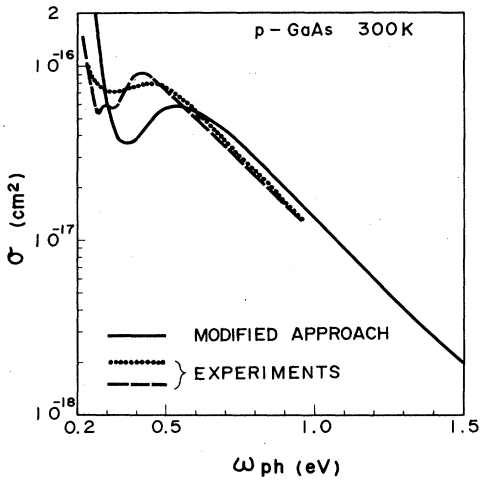

FIG. 6. σ's obtained as functions of ω_{ph} from the modified approach (——) with $n_A \leq 2\times10^{18}$ cm^{-3} and from experiments with $n_A = 6.8\times10^{17}$ cm^{-3} (— —) and 10^{18} cm^{-3} (· · ·) for p-type GaAs at 300 K.

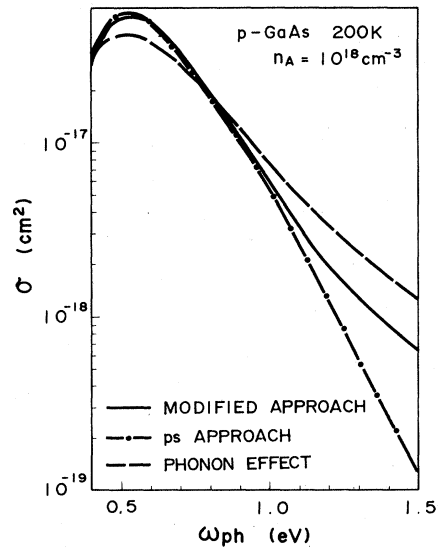

FIG. 7. σ's calculated as functions of ω_{ph} in the modified approach (——), the ps approach (—·—), and the phonon-effect approach (— — —) for p-type GaAs with $n_A = 10^{18}$ cm^{-3} at 200 K.

sorption cross section, even on other materials such as InP and InGaAsP. However, there is an experimental value[16] of $\alpha=12$ cm^{-1} at a photon energy close to the band-gap energy, i.e., 1.42 eV, which has been determined from a laser operation at 300 K. A theoretical analysis made with a laser-simulation program[17] on the basis of the results in Fig. 5 has led to $\alpha=9$ cm^{-1} for the given laser conditions. Thus agreement between the theory and experiment is good.

A strong indication of inadequacy of the ps approach at high photon energies is seen in Fig. 7, where the absorption cross sections at 200 K are shown for three different approaches, i.e., the modified approach (a solid line), the ps approach (a dotted-dashed line), and the phonon-effect approach (a dashed line). It is seen that the ps approach gives exceedingly smaller values than the other approaches, especially at high energies. Noting that the n_A value considered is so small as to make the impurity effect negligible, it is considered that the phonon effect is not properly incorporated into the ps approach.

In view of this fact and of the agreement between the theory and experiments, it is concluded that the modified approach offers a practical means of analyzing doped semiconductors in a range where the phonon-scattering effect as well as the impurity-scattering effect is important.

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[1]M. Takeshima, Jpn. J. Appl. Phys. **23**, 428 (1984).
[2]H. Y. Fan, in *Semiconductors and Semimetals,* edited by R. K. Willardson and A. C. Beer (Academic, New York, 1967), Vol. 3, Chap. 3.
[3]M. Takeshima, Phys. Rev. B **23**, 6625 (1981).
[4]M. Takeshima, Phys. Rev. B **25**, 5390 (1982).
[5]M. Takeshima, Phys. Rev. B **27**, 7524 (1983).
[6]M. Takeshima, Phys. Rev. B **30**, 4540 (1984).
[7]V. L. Bonch-Bruevich, in *Semiconductors and Semimetals,* Ref. 2, Vol. 1, Chap. 4.
[8]M. Takeshima, Phys. Rev. B **27**, 2387 (1983).
[9]M. Takeshima, J. Appl. Phys. **56**, 49 (1984).
[10]E. O. Kane, in *Semiconductors and Semimetals,* Ref. 2, Vol. 1, Chap. 3.
[11]J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **14**, 556 (1976).
[12]M. Newberger, in III-V *Semiconducting Compounds* (Plenum, New York, 1971).
[13]S. Doniach and E. H. Sondheimer, in *Green's Function for Solid State Physicists* (Benjamin, Massachusetts, 1974).
[14]R. Braunstein, J. Phys. Chem. Solids **8**, 280 (1959).
[15]C. H. Henry, R. A. Logan, F. R. Meritt, and J. P. Luongo, IEEE J. Quantum Electron. **QE-19**, 947 (1983).
[16]E. Pinkas, B. I. Miller, I. Hayashi, and P. W. Foy, J. Appl. Phys. **43**, 2827 (1972).
[17]M. Takeshima (unpublished).