

Low-Level Interband Absorption in Phosphorus-Rich Gallium Arsenide-Phosphide

P. J. DEAN, G. KAMINSKY, AND R. B. ZETTERSTROM
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
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The optical absorption edge of GaP is influenced in two principal ways when a few percent of the phosphorus atoms are replaced by arsenic. Besides the uniform decrease of the indirect band gap, the mixed crystal exhibits an extra absorption component. It is shown that this component is due to the no-phonon creation of free excitons and free-electron-hole pairs. Momentum is conserved through scattering at the arsenic impurities. The cross section for this process apparently decreases with increasing kinetic energy of the free excitons. In addition, the matrix element for indirect transitions assisted by the emission of LA phonons is enhanced by the decrease in the X_{1c} - Γ_{1c} energy separation in the mixed crystal. The replacement of phosphorus by arsenic in GaP is a relatively minor perturbation. Unlike the case of nitrogen in GaP, there is no bound state. The near-threshold absorption due to the arsenic-induced creation of free particles is only $\sim 0.1\%$ of that due to nitrogen substituents.

I. INTRODUCTION

THE forbidden gap of the mixed III-V semiconductor $\text{GaAs}_x\text{P}_{1-x}$ remains an indirect type for $x \lesssim 0.6$.¹ Interband optical absorption cannot occur in a perfect stoichiometric indirect-gap semiconductor except for optical transitions involving the emission or absorption of phonons. The theoretical form of the indirect absorption edge for phonon-assisted transitions involving the creation of free excitons is due to Elliott.² Since the exciton is a stable quasiparticle, Elliott predicted that the absorption coefficient α for a component involving the absorption or emission of a particular momentum-conserving (MC) phonon has a dependence on the photon energy $h\nu$ determined by the density-of-states function for a single particle, namely,

$$\alpha = \text{const} \times (h\nu - E_0)^{1/2}, \quad (1)$$

where E_0 is the threshold energy of the given component. The photocreation of unbound pairs of electrons and holes can occur at $h\nu > E_0 + E_x$, where E_x is the internal binding energy of the free exciton. For energies not too far above the threshold ($E_0 + E_x$) compared with the energy E_x , the form of this absorption process is given by²

$$\alpha = \text{const} \times (h\nu - E_0 - E_x)^{3/2}. \quad (2)$$

The constants in Eqs. (1) and (2) involve the phonon energy $\hbar\omega$ and temperature T , but are nearly independent of temperature for the emission of phonons when $\hbar\omega \gg kT$, where k is Boltzmann's constant. This theory was first used to interpret the low-level optical absorption edges of refined germanium and silicon.³ Since then absorption processes of this type have been demonstrated in a number of semiconductors, including GaP.⁴

Additional absorption processes occur in an indirect-gap semiconductor containing impurities or crystal defects, particularly those which exhibit a large scattering cross section for one or other type of free carrier and therefore for free excitons. These processes have been discussed recently in connection with the optical properties of nitrogen in GaP.⁵ Of particular interest here are the continua commencing at the energy gap E_g and at $E_{gx} = E_g - E_x$. These absorption continua represent, respectively, the *no-phonon* creation of free-electron-hole pairs and of free excitons. These processes, forbidden in the perfect crystal, are possible in the vicinity of the nitrogen atom, since momentum can be conserved in the transition through scattering at this impurity. Indeed, it has recently been shown that the cross section for this process is resonantly large in GaP:N, because of the existence of a shallow bound state for the electron at the nitrogen atom. Each nitrogen atom induces about 7000 times more *free-particle* absorption at ~ 0.04 eV above E_{gx} than the phosphorus atom it replaces. In practice, the shapes of these absorption components are partially masked by strong overlapping absorption due to the creation of bound excitons at the nitrogen atoms with phonon emission. Pronounced distortions due to interference between these two nitrogen-induced absorption processes also occur.⁶

Bound electronic states are not produced by isolated arsenic atoms substituting for phosphorus in GaP. Impurity-induced absorption due to the no-phonon and phonon-assisted creation of free particles can still occur, however. These absorption processes are investigated in the present paper in the mixed III-V semiconductor $\text{GaAs}_x\text{P}_{1-x}$, for small x , $\lesssim 0.15$. It is shown that the arsenic-induced free-particle absorption is much weaker than the corresponding nitrogen-induced absorption in GaP, because the scattering cross section of the impurity atom is small in the absence of a bound state. The form of the arsenic-induced free-particle absorption is discussed.

¹ D. A. Cusano, G. E. Fenner, and R. O. Carlson, *Appl. Phys. Letters* **5**, 144 (1964).

² R. J. Elliott, *Phys. Rev.* **108**, 1384 (1957).

³ This work has been reviewed by T. P. McLean, *Progress in Semiconductors* (Wiley-Interscience, Inc., New York, 1960), Vol. 5, p. 55.

⁴ P. J. Dean and D. G. Thomas, *Phys. Rev.* **150**, 690 (1966).

⁵ R. A. Faulkner, *Phys. Rev.* **175**, 991 (1968).

⁶ J. J. Hopfield, P. J. Dean, and D. G. Thomas, *Phys. Rev.* **158**, 748 (1967).

II. EXPERIMENTAL

A. Crystal Growth

It was not possible to grow $\text{GaAs}_x\text{P}_{1-x}$ mixed crystals from gallium solution for this work, since large compositional inhomogeneities occur because of the change in liquid composition in the closed system as the solid crystals are formed, and also because of the relatively wide temperature range over which growth may occur. Mixed crystals of suitably uniform composition were prepared from the vapor phase. A polycrystalline ingot of GaP was placed at $\sim 1100^\circ\text{C}$ in a stream of wet hydrogen. A mixture of 5% AsH_3 in H_2 gas was introduced downstream from the GaP source⁷ through a high-purity alumina tube. Mixed crystals of $\text{GaAs}_x\text{P}_{1-x}$ grew on the walls of the fused silica furnace insert tube at $\sim 60^\circ\text{C}$ below the temperature of the GaP source. The compositional parameter x was varied in the range 0.005–0.15 by suitable adjustment of the flow rate of the AsH_3 - H_2 gaseous mixture. Predominantly needlelike crystal growth was obtained by this method. The side faces of the as-grown crystals were usually rough.

The compositions of the mixed crystals were determined by x-ray fluorescence microanalysis, using pure GaAs as a reference. The homogeneity of the crystals was checked in this way, and also from the threshold energies of absorption edge spectra recorded from different regions of the larger crystals. With the crystals available, the sensitivity limit of the x-ray fluorescence analysis corresponded to $x \sim 0.001$.

B. Optical Measurements

Most of the transmission measurements were made along the axis of single-crystal vapor-grown needles of

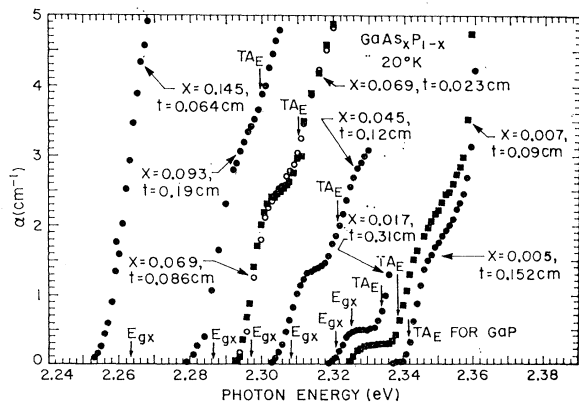


FIG. 1. Low-level absorption edge spectra of several single crystals of $\text{GaAs}_x\text{P}_{1-x}$ with the indicated compositions. The thicknesses of the crystals used are also given on each curve. The absorption spectrum on the extreme right indicated very little arsenic, $x \leq 0.001$, but the x-ray fluorescence analysis indicated a significantly larger value for this crystal.

⁷ The techniques used to grow doped needles of GaP by the wet-hydrogen transport method have been discussed by C. J. Frosch, J. Electrochem. Soc. 111, 180 (1964); W. C. Ellis, C. J. Frosch, and R. B. Zetterstrom, J. Crystal Growth 2, 61 (1968).

$\text{GaAs}_x\text{P}_{1-x}$ with polished end faces. Measurements were also made between polished side faces of some of these crystals in order to determine a higher range of absorption coefficient. The crystals were placed within apertures in molybdenum masks and mounted in such a way as to be as free of strain as possible. They were cooled to $\sim 20^\circ\text{K}$ in a stream of cold helium gas. The optical source was a 100-W tungsten strip-filament projector lamp. Light transmitted by the needles was focused into the entrance slit of a Spex $f/6.8$ Czerny-Turner grating monochromator fitted with an EM1 9558 QA photomultiplier mounted in a thermoelectric cooler. The transmission spectra were recorded continuously on a Moseley recorder, and the data were reduced by point-by-point analysis.

Many of the crystals were too small to enable an accurate absolute measurement to be made according to the standard equation for the transmission T which takes account of multiple internal reflections:

$$T = I_T/I_0 = (1-R)^2 e^{-\alpha t} / (1-R^2 e^{-2\alpha t}), \quad (3)$$

where R is the external reflectivity, α is the absorption coefficient, t the thickness of the crystal, and I_0 and I_T are the incident and transmitted light intensities. The technique discussed in Ref. 4 was therefore used for most of the measurements. The slowly varying absorption just below the onset of interband absorption was discounted by a transformation of Eq. (3) in which I_0 is replaced by I_{T^1} , the transmitted intensity for zero interband absorption. The intensity I_{T^1} was obtained by a smooth extrapolation to higher energy of the transmitted signal recorded immediately below the threshold of interband absorption. The transformed relation between I_T and α is

$$T^1 = I_T/I_{T^1} = (1-R^2) e^{-\alpha t} / (1-R^2 e^{-2\alpha t}). \quad (4)$$

Absolute absorption measurements were possible on a few exceptionally large vapor-grown crystals. Measurements made in this way on one of these compared very well with the $\alpha, h\nu$ relationship for interband absorption determined from Eq. (4), even though a "background" absorption coefficient of $\sim 9\text{ cm}^{-1}$ occurred just below the interband edge. Much of the decrease in transmission described by this background absorption may be due to light scattering within the mixed crystals.

III. RESULTS AND DISCUSSION

A. General Features of Absorption Edge of $\text{GaAs}_x\text{P}_{1-x}$

The extra component induced in the interband absorption of $\text{GaAs}_x\text{P}_{1-x}$ is clearly shown in Fig. 1 for crystals containing small concentrations of arsenic. The arrows denote the anticipated position of the exciton energy gap E_{gx} and the threshold of the absorption component due to the creation of free excitons with the

emission of transverse-acoustical (TA) phonons.⁸ These arrows have been positioned in accordance with the shift of the indirect gap with alloy composition published by Cusano *et al.*,^{1,9} using arsenic concentrations determined for the present samples by x-ray fluorescence. The agreement between the arrows and the thresholds of the observed components is consistent with the stated accuracy of the x-ray compositional analysis (Sec. II A). The thresholds of the absorption components become poorly defined with increase in the mole fraction of GaAs above a few percent. This is presumably due to statistical fluctuations in alloy composition in the environment of particular As or P atoms. This effect will be enhanced by the clustering which has been detected through studies of the vibrational spectra of $\text{GaAs}_x\text{P}_{1-x}$.¹⁰

The linear connection between the excess absorption and the compositional parameter x in $\text{GaAs}_x\text{P}_{1-x}$, shown in Fig. 2, identifies this absorption with transitions induced by the arsenic atoms. The extra absorption is smoothly varying and occurs only above E_{gx} , unlike that observed in GaP:N ,⁶ showing that arsenic atoms do not introduce bound electronic states in GaP. According to Figs. 1 and 2, each arsenic atom in $\text{GaAs}_x\text{P}_{1-x}$ introduces nearly seven times as much free-particle absorption at an energy 0.04 eV above the exciton band gap as each phosphorus atom in GaP. Thus the impurity-induced free-particle absorption due to arsenic is ~ 1000 times weaker than that due to nitrogen (Sec. I). This large difference is to be expected in the absence of a shallow bound state due to arsenic in GaP according to the interpretation of the properties of nitrogen in GaP given in Ref. 5. The large difference between the properties of these two impurities is also qualitatively consistent with the view that the optical properties of isoelectronic substituents are predominantly due to differences in the pseudopotentials of the host and impurity atoms, and are very sensitive to these differences.⁵ Phillips has recently shown that, in general, the primary effect of the electronegativity difference will be greatly reduced by the electronic effect of lattice deformation around the impurity atom.¹¹ Arsenic is

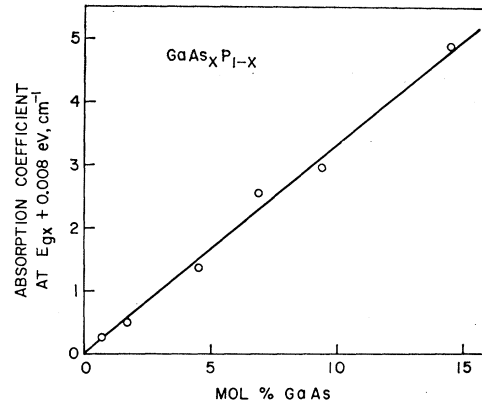


Fig. 2. Strength of the absorption 8 meV above the exciton energy gap E_{gx} in $\text{GaAs}_x\text{P}_{1-x}$ mixed crystals as a function of the compositional parameter x . This absorption is due to the no-phonon creation of free excitons induced by the arsenic atoms.

very slightly less electronegative than phosphorus.¹² However, its behavior in semiconductors is anomalous in that arsenic donors possess appreciably larger central cell corrections than phosphorus, both in silicon¹³ and in germanium.¹⁴ Arsenic is therefore likely to produce an attractive impurity potential for electrons in GaP, although this effect should be much weaker than for nitrogen. In the next section, we show that the excess absorption in $\text{GaAs}_x\text{P}_{1-x}$ is largely due to the no-phonon creation of free excitons and free-electron-hole pairs in the vicinity of the arsenic atoms.

B. Shape and Strength of the Arsenic-Induced Interband Absorption

The broadening effect mentioned in Sec. III A makes it difficult to investigate the form of the arsenic-induced absorption in alloys containing high concentrations of arsenic. On the other hand, relatively thick crystals of macroscopically homogeneous composition are required for accurate analysis of the extra absorption at low concentrations of arsenic. Figure 3 shows that the no-phonon absorption induced by the arsenic rises from the threshold at E_{gx} more rapidly than the form of Eq. (1) and is better described by the expression

$$\alpha = \text{const} \times (h\nu - E_{gx})^{1/4}. \quad (5)$$

Equation (5) suggests that the scattering cross section of the arsenic isoelectronic centers decreases significantly with the kinetic energy E_{KE} of the free particle, possibly as $E_{KE}^{-1/4}$. This result contrasts with data on $\text{AgCl}_2\text{Br}_{1-x}$ alloys,¹⁵ where the absorption component due to the no-phonon creation of free excitons was found to have the form of Eq. (1).

⁸ The threshold energies were not sufficiently well defined at the larger values of the compositional parameter x to enable the reduction in the TA phonon energy anticipated for the mixed crystal to be established.

⁹ It was assumed that $E_{gx} = 2.339$ eV in GaP at 20°K or below (Ref. 4) and that the $\Gamma_{15v} \rightarrow X_{1c}$ indirect band gap decreases by 0.45 eV as x varies from 0 to 1 in $\text{GaAs}_x\text{P}_{1-x}$ (Ref. 1, 80°K data). The latter result was obtained from the peak energies of cathodoluminescence bands, and corroboration by other means would be useful. I. Balslev [Phys. Rev. 173, 762 (1968)] has recently measured the energy difference $\Gamma_{1c} \rightarrow X_{1c}$ in GaAs to be 0.43 ± 0.015 eV at 80°K. This result, together with the 80°K values of E_g for GaP (2.332 ± 0.002 eV from Ref. 4) and GaAs [1.513 ± 0.0015 eV from M. D. Sturge, *ibid.* 127, 768 (1962)], implies that the $\Gamma_{15v} \rightarrow X_{1c}$ energy gap increases by 0.39 ± 0.015 eV between GaAs and GaP. Unfortunately, this value agrees less well with the data in Fig. 1 than the earlier result from Ref. 1.

¹⁰ H. W. Verleur and A. S. Barker, Jr., Phys. Rev. 149, 715 (1966).

¹¹ J. C. Phillips, Phys. Rev. Letters 22, 285 (1969).

¹² W. Gordy and W. J. O. Thomas, J. Chem. Phys. 24, 439 (1956).

¹³ R. L. Aggarwal and A. K. Ramdas, Phys. Rev. 140, A1246 (1965).

¹⁴ D. K. Wilson and G. Feher, Bull. Am. Phys. Soc. 5, 60 (1962); J. H. Reuszer and P. Fisher, Phys. Rev. 135, A1125 (1964).

¹⁵ B. L. Joesten and F. C. Brown, Phys. Rev. 148, 919 (1966).

According to the absorption edge of pure GaP,⁴ the threshold of the absorption due to the no-phonon creation of unbound-electron-hole pairs should commence ~ 10 meV above the threshold of the corresponding free-exciton component. This component is not evident in Figs. 1 and 3. Presumably, the threshold of the predicted form $(E-E_0)^{3/2}$ [Eq. (2)] is masked by the effects of both the compositional broadening and the energy-dependent scattering cross section of the arsenic atoms in the mixed crystals. We believe that the absorption component due to the arsenic-induced creation of free-electron-hole pairs is subsumed in the high-energy tail of the free-exciton no-phonon component. This implies that the deviation of the latter component from Eq. (1) is even more pronounced than suggested in the previous paragraph. According to the calculations for GaP:N in Ref. 5, the sum of the absorption processes due to the no-phonon creation of free excitons and of free-electron-hole pairs does indeed rise slowly with energy for $h\nu \gg E_g$, roughly as the form in Eq. (5). The absorption due to the creation of free excitons decreases with increasing energy in this range. The near-threshold form of the nitrogen-induced absorption is complicated by cross-channel interference with absorption due to the creation of bound electrons and free holes, a process which does not occur for arsenic substituents.

The arsenic impurities should also induce phonon-assisted interband transitions. The corresponding absorption components are energetically indistinguishable from absorption due to phosphorus. Both sets of absorption features are shifted due to the decrease in band gap of the mixed crystal compared with GaP. Figure 4 shows that the excess absorption in an alloy containing 6.9-mole % GaAs is largely due to the no-phonon transitions induced by the arsenic atoms, even well above the onset of phonon-assisted transitions. The fluctuations in the difference absorption curve near the thresholds of the TA_E and LA_E phonon-assisted components is due to the compositional broadening near

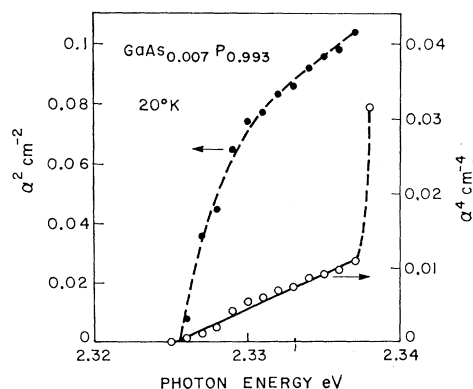


FIG. 3. α^2 and α^4 versus $h\nu$ for $\text{GaAs}_{0.007}\text{P}_{0.993}$. The appropriate ordinate scales are indicated by the arrows. The disorder-induced broadening is relatively small for such small arsenic concentrations, but the absorption is also weak.

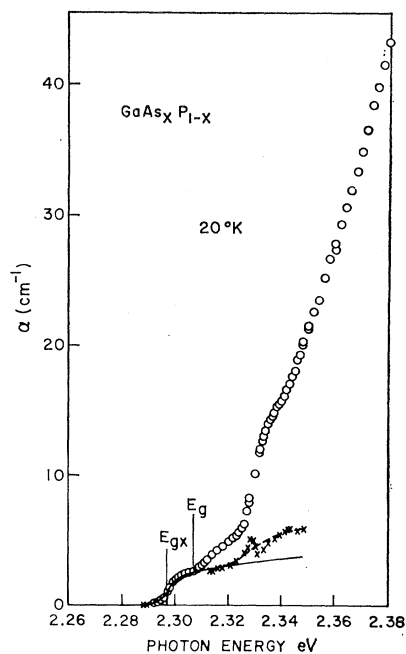


FIG. 4. Low-level absorption edge spectrum from a $\text{GaAs}_{0.069}\text{P}_{0.931}$ single crystal (O points). This spectrum was obtained from measurements on three pieces from the same single crystal 0.023, 0.086, and 0.65 cm thick. The lower X points show the difference between this curve and the absorption edge spectrum of pure GaP translated 31.5 meV to lower energy to allow for the decrease in the $\Gamma_{15_v} \rightarrow X_{1_c}$ energy gap of the mixed crystal. The lower smooth curve is a plausible fit of the form $(h\nu - E_{gx})^{1/4}$ to the excess absorption, due both to the no-phonon creation of free excitons and free-electron-hole pairs. The difference between this curve and the dashed curve denotes the excess absorption due to LA phonon-assisted transitions in the mixed crystal, smoothed to remove the effects of compositional broadening (see text).

these thresholds in the mixed crystal. This broadening was not present in the displaced absorption spectrum of GaP which was used in the subtraction. The energy displacement of the GaP absorption data was adjusted according to the threshold of the no-phonon component of the $\text{GaAs}_{0.069}\text{P}_{0.931}$ data obtained from the fit to the $(h\nu - E_{gx})^{1/4}$ form given in Fig. 4.

Compositional broadening effects are probably mainly responsible for the small deviations of the smoothed absorption difference curve above the $(h\nu - E_{gx})^{1/4}$ component apparent in Fig. 4 near 2.335 eV. This deviation increases abruptly near the threshold of the LA_E phonon-assisted absorption component. Indirect transitions involving electron scattering through the virtual intermediate state derived from the Γ_1 conduction-band minimum, which are favored in GaP from energy considerations, are allowed by symmetry only for the LA phonon.⁴ The increased strength of the LA phonon-assisted transitions shown in Fig. 4 is due to the increase in the transition probability resulting from the decrease in the $\Gamma_1 \rightarrow X_1$ energy difference in the $\text{GaAs}_{0.069}\text{P}_{0.931}$ mixed crystal. The increase in the strength of this absorption component at 5 meV above its threshold for $\text{GaAs}_{0.069}\text{P}_{0.931}$ compared with GaP, calculated using

the Elliott theory for indirect transitions² according to the energy-band structure for the $\text{GaAs}_x\text{P}_{1-x}$ mixed-crystal system given in Ref. 1 and the GaP absorption data in Ref. 4, is $\sim 1.5 \text{ cm}^{-1}$. This calculated value is in good agreement with the measured absorption excess in the LA_B phonon-assisted component shown in Fig. 4.

IV. SUMMARY

Pronounced optical absorption appears just above the exciton energy gap E_{gx} of the indirect-gap semiconductor GaP in the presence of a few mole % of GaAs. The most prominent absorption component is due to the creation of free excitons and free-electron-hole pairs. The threshold for the latter process is not clearly defined in the mixed crystals. Momentum is conserved in this transition through scattering in the localized potential of the arsenic impurities. The decrease in the energy difference between the Γ_1 and X_1 conduction-

band minima in $\text{GaAs}_x\text{P}_{1-x}$ compared with GaP also induces extra indirect absorption in the mixed crystal associated with the emission or absorption of momentum-conserving LA phonons. The free-particle absorption, measured at an arbitrarily chosen energy 0.04 eV above E_{gx} , is ~ 7 times larger for each arsenic atom than for the phosphorus atom it replaces, but is only $\sim 0.1\%$ of the corresponding absorption due to nitrogen substituents in GaP. These results demonstrate the high sensitivity of the optical absorption process to the difference between the electronic properties of the host and substituent atoms.

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Note on Optical Mixing by Mobile Carriers in Semiconductors*

B. S. KRISHNAMURTHY AND V. V. PARANJAPE

Department of Physics, Lakehead University, Port Arthur, Ontario, Canada

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It is shown that nonlinearity due to energy dependence of the carrier momentum relaxation time in semiconductors may arise even when the electrons have the same temperature as the lattice. This leads to modifications in the results of a recent paper.

IN a recent paper by Kaw,¹ it has been shown that the energy dependence of the carrier momentum relaxation time may contribute to optical mixing even in parabolic-band-type semiconductors. In this paper we point out that the model used by the author¹ is valid when electron temperature T_e is very much greater than lattice temperature T , while in the warm-electron situation $(T_e - T)/T \ll 1$ (as in Ref. 1) the calculations require modifications.

We start with the equation of motion for an average carrier in the form

$$\partial \mathbf{V} / \partial t + \mathbf{V} / \tau(\bar{\epsilon}) = -e\mathbf{E} / m, \quad (1)$$

where $\mathbf{E} = \mathbf{E}_1 \exp i\omega_1 t + \mathbf{E}_2 \exp i\omega_2 t + (\text{complex conjugate})$ is the electric field due to laser beams, \mathbf{V} is the average carrier velocity, m is the effective mass, and $\tau(\bar{\epsilon})$ is the carrier momentum relaxation time which depends on the average energy of the carrier $\bar{\epsilon}$. In the presence of laser beams, the average energy at time t may be written

$$\bar{\epsilon} = \frac{3}{2} k T_e + \frac{1}{2} m V^2, \quad (2)$$

where the second term in the above equation is the energy associated with the drift velocities of the carriers. This term is usually disregarded if electrons are hot, i.e., $T_e \gg T$, but in the case of warm electrons, it has been demonstrated by Paranjape and Alba² that the term is important and can lead to electron cooling by a dc electric field. Here it is shown that inclusion of the term produces significant changes in the results of Ref. 1. In the notations of Ref. 1 we write

$$1/\tau = (1/\tau_0) \{ 1 - \frac{1}{2} n [(T_e/T) - 1] - m V^2 / 3kT \}, \quad (3)$$

where n is an integer.

The electron temperature T_e is determined by the energy balance equation which in view of Eq. (2) is given by

$$d\bar{\epsilon}/dt = -e\mathbf{V} \cdot \mathbf{E}, \quad (4)$$

where we have neglected the energy loss of the electrons to the lattice. This simplifying assumption as in Ref. 1 is correct provided ω_1 , ω_2 , and $\omega_1 - \omega_2$ are very much greater than the reciprocal of the energy relaxation time. We now develop \mathbf{V} and T as a sum of com-

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