

Radiative recombination in heavily doped *p*-type germanium

J. Wagner and L. Viña

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Federal Republic of Germany*

(Received 23 May 1984)

Low-temperature photoluminescence studies on heavily doped *p*-type germanium are reported. In addition to the indirect-band-gap (0.75 eV) luminescence, direct recombination of nonthermalized minority carriers located at the conduction-band minimum at point  $\Gamma$  is observed. The direct recombination occurs across the gaps  $E_0$  and  $E_0 + \Delta_0$  (0.89 and 1.19 eV, respectively) and resonates strongly for exciting photon energies close to the energy gap  $E_0$ . The emission across the gap  $E_0$  can be described as a mixture of band-to-band transitions with and without momentum conservation. From the luminescence spectra the shift of the indirect band gap as well as the direct band gap  $E_0$  is determined as a function of carrier concentration and compared to full pseudopotential band-structure calculations.

## I. INTRODUCTION

The effect of heavy doping on the electronic properties of a semiconductor can be described, besides the band tailing due to the random distribution of the dopant atoms, in terms of a reduction of the band gap.<sup>1</sup> For doping levels so high that the material becomes degenerate, a filling of the conduction or valence band occurs (for *n*- or *p*-type material, respectively).<sup>1</sup> The reduction of the band gap as well as the charge-carrier distribution within the bands can be studied by photoluminescence via the radiative recombination of photoexcited minority carriers.<sup>2,3</sup>

Most of the luminescence work reported for heavily doped germanium deals with *n*-type material.<sup>2,4-7</sup> Not much information exists about the luminescence properties of heavily doped *p*-type germanium.

In this paper, low-temperature photoluminescence (PL) spectra of *p*-type germanium doped with Ga at concentrations ranging from  $6 \times 10^{18}$  to  $7.8 \times 10^{19} \text{ cm}^{-3}$  are reported. The PL spectra show, besides the recombination band from electrons in the lowest indirect conduction-band minima at the *L* point (see Fig. 1), luminescence from nonthermalized electrons located at the direct-conduction-band minimum. Direct-gap recombination has been reported in the literature<sup>8-10</sup> for highly photoexcited pure germanium. The direct-gap luminescence found in the present study exhibits, however, a different dependence on excitation intensity and is also observed under very low optical excitation. This finding allows us to study not only the lowest indirect-band-gap energy but also the direct gap  $E_0$  as a function of carrier concentration. The  $E_0$ -gap emission, which resonates strongly for exciting photon energies close to the energy gap  $E_0$ , can be described as a mixture of band-to-band transitions with and without momentum conservation.

Section II of this paper gives a description of the experimental details. A short discussion of the theory used to calculate the band-gap shifts upon doping is presented in Sec. III. Section IV deals with the experimental results

and their interpretation and finally the conclusions are given in Sec. V.

## II. EXPERIMENT

The samples used in the present study were bulk doped with gallium. The carrier concentration ranges from  $6 \times 10^{18}$  to  $7.8 \times 10^{19} \text{ cm}^{-3}$  as determined from room-temperature conductivity and from the plasma frequency, which was obtained from the minimum in the infrared reflectivity. The surfaces of the samples were polished.

The cooling of the samples to 5 K was accomplished by means of He exchange gas. The luminescence was excited either by several visible and near-infrared lines of a  $\text{Kr}^+$  laser or by the 1064- or 1319-nm line of a  $\text{Nd}^{3+}$ -YAG (yttrium aluminum garnet) laser. The luminescence light was dispersed by a 1-m double monochromator and detected either with a cooled intrinsic Ge photodiode or with a PbS detector.

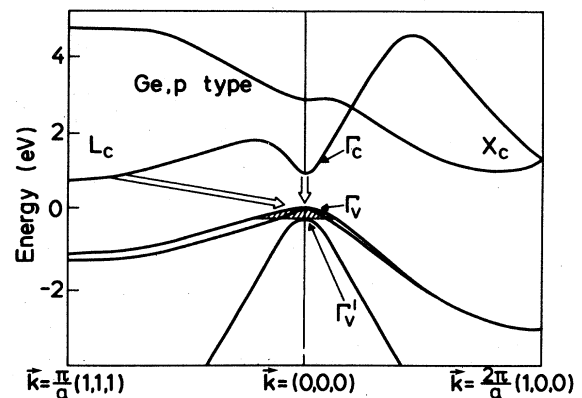


FIG. 1. Band structure of Ge. The luminescence transitions observed in heavily doped *p*-type material are indicated by arrows. The band separations, referring to low temperature and pure Ge, are  $E_G = 0.744 \text{ eV}$  ( $L_c \rightarrow \Gamma_v$ ),  $E_0 = 0.889 \text{ eV}$  ( $\Gamma_c \rightarrow \Gamma_v$ ), and  $E_0 + \Delta_0 = 1.189 \text{ eV}$  ( $\Gamma_c \rightarrow \Gamma'_v$ ).

## III. THEORY

The renormalized band structure of a semiconductor in the presence of impurities can be described by the Hamiltonian<sup>11-13</sup>

$$\hat{H} = \hat{H}_e + \hat{H}_{ei}, \quad (1)$$

where

$$\hat{H}_e = \sum_{\vec{k}, n} e_{\vec{k}n} C_{\vec{k}n}^\dagger C_{\vec{k}n} \quad (2)$$

describes the band structure of the pure semiconductors and the carrier-impurity part of the Hamiltonian is

$$\hat{H}_{ei} = \sum_{\vec{k}, n, \vec{k}', n'} \langle \vec{k}'n' | V_I | \vec{k}, n \rangle C_{\vec{k}'n'}^\dagger C_{\vec{k}n}. \quad (3)$$

$V_I$  represents the difference between the crystal potential with and without impurities present,  $C_{\vec{k}n}^\dagger$  and  $C_{\vec{k}n}$  are the creation and annihilation operators for an electron with energy  $e_{\vec{k}n}$  and wave vector  $\vec{k}$  in band  $n$ , respectively.

Assuming that the substitutional impurities are randomly distributed, the energy bands renormalized by the presence of the impurities are given by the zeros of<sup>11,13</sup>

$$\det[(z - e_{\vec{k}n})\delta_{nn'} - \Sigma(\vec{k}, n, n'; z)] = 0, \quad (4)$$

where  $\Sigma(\vec{k}, n, n'; z)$  is the self-energy matrix. In the case of small self-energy, Rayleigh-Schrödinger perturbation theory can be used to obtain the roots of Eq. (4); up to second order in the impurity potential and neglecting multiple-scattering effects, the result is a complex energy.<sup>11,13</sup>

$$E_{\vec{k}n} = e_{\vec{k}n} + \Delta_{\vec{k}n} + \frac{i}{2\tau_{\vec{k}n}} = e_{\vec{k}n} + \Delta_{\vec{k}n}^{(1)} + \Delta_{\vec{k}n}^{(2)} + \frac{i}{2\tau_{\vec{k}n}}. \quad (5)$$

$\Delta_{\vec{k}n}^{(1),(2)}$  is the shift in the band structure in first- (second-) order perturbation theory and  $\tau_{\vec{k}n}$  is a lifetime. The  $e_{\vec{k}n}$  have been obtained from a full pseudopotential band-structure calculation, where the local pseudopotential of Cohen and Bergstresser<sup>14</sup> was used.

We have evaluated the first-order term of Eq. (8) ( $\Delta_{\vec{k}n}^{(1)}$ ) in the "virtual-crystal approximation," i.e., by exact diagonalizing<sup>13</sup> of the Hamiltonian matrix with averaged pseudopotentials,

$$V(G) = (1-x)V_G(\text{Ge}) + xV_G(X^{\text{III}}). \quad (6)$$

The form factors of the group-III acceptors  $X^{\text{III}}$  were estimated from the corresponding values for III-V compounds.<sup>13-15</sup> Averaging the results for B, Al, Ga, and In we obtained a linear blue shift of  $32 \times 10^{-24}$  eV cm<sup>-3</sup> for the gap  $E_0$  and a linear red shift of  $7 \times 10^{-24}$  eV cm<sup>-3</sup> for the indirect gap  $E_G$ .

For the dopant concentrations considered here ( $10^{19}$ – $10^{20}$  cm<sup>-3</sup>), these shifts are about one order of magnitude smaller than the second-order shifts given by

$$\Delta_{\vec{k}n}^{(2)} = N \sum_{\substack{\vec{q}, m \\ q \neq 0}} \frac{|\langle \vec{k}, n | V^{\text{imp}} | \vec{k} + \vec{q}, m \rangle|^2}{(e_{\vec{k}n} - e_{\vec{k} + \vec{q}, m})}, \quad (7)$$

with  $N$  representing the number of ionized impurities.

For  $V^{\text{imp}}$  we have used a screened "hydrogenic" Coulomb potential.<sup>13</sup> Equation (7) was computed by performing a Hilbert transform of the imaginary part of Eq. (5) and this through direct integration over the Brillouin zone<sup>11,13</sup> using the tetrahedron method.<sup>16</sup>

Red shifts for both gaps were obtained in this case. The total shifts arise from a down-shift of the conduction band and an up-shift of the valence band. A slightly larger red shift is obtained for the gap  $E_0$  than for the indirect gap  $E_G$ . This is partially compensated by the first-order shifts (blue shift in the case of  $E_0$  and red for  $E_G$ ).

In addition to the band shifts discussed above, the exchange energy of the holes causes a further reduction of both  $E_G$  and  $E_0$ . The numerical values for the hole-exchange energy, taken from the work of Brinkman and Rice,<sup>17</sup> amount to about 10% of the second-order band shift. The calculated total gap reduction, which is the sum of the first- and second-order terms plus the hole exchange energy, will be compared with the experimental data in Sec. IV.

## IV. RESULTS AND DISCUSSION

## A. Indirect luminescence

Typical indirect-luminescence spectra of *p*-type germanium are displayed in Fig. 2 for various carrier concentrations. This luminescence is due to the recombination of photoexcited electrons in the *L*-point conduction-band minima with holes in the valence band at the  $\Gamma$  point (see Fig. 1). The emission band consists of the no-phonon (NP) replica at shorter wavelengths and the momentum-conserving longitudinal acoustic (LA) phonon replica at longer wavelengths as can be seen from the PL spectra of the samples containing  $6 \times 10^{18}$  and  $2 \times 10^{19}$  holes/cm<sup>3</sup>. For the most heavily doped sample ( $7.8 \times 10^{19}$  holes/cm<sup>3</sup>), these two replicas cannot be resolved further and the indirect emission band starts to overlap with the direct emission band at higher energies (see Sec. IVB). The high-energy cutoff of the luminescence indicates the energy of the optical gap  $E_G + E_F$ , which is the minimum photon energy required to excite an electron from the valence band to the conduction band. Here  $E_G$  is the energy gap between the top of the valence band and the bottom of the conduction-band minima at the *L* point and  $E_F$  is the filling of the valence band. The low-energy edge of the luminescence band represents the band-gap energy  $E_G$  minus the LA-photon energy of 27 meV.

Now we shall discuss the line shape of the indirect-luminescence spectra. For indirect band-to-band transitions, where momentum conservation is fulfilled by phonon participation (LA replica) or by impurities (NP replica), the emission line shape  $I(h\nu)$  can be expressed by the convolution of the densities of states  $D_e(E)$  and  $D_h(E)$  weighted by the distribution functions  $f_e(E)$  and  $f_h(E)$

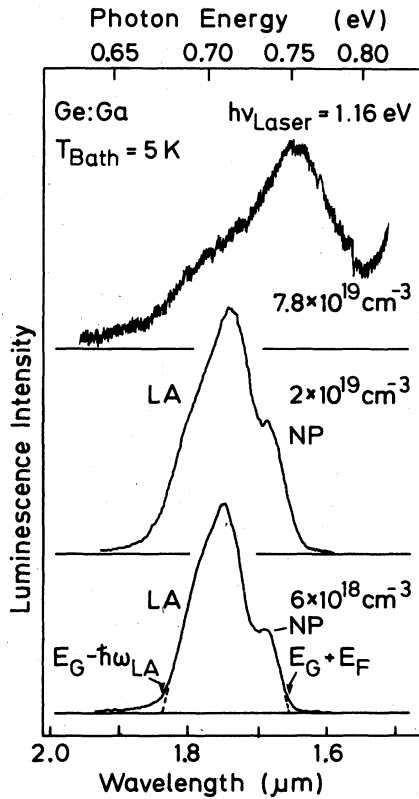


FIG. 2. Indirect PL spectra of gallium-doped germanium for various hole concentrations as indicated. Arrows indicate the high-energy cutoff of the NP line  $E_G + E_F$  and the low-energy edge of the LA replica  $E_G - \hbar\omega_{LA}$ . The spectra were recorded using a PbS detector at a spectral resolution of 32 Å.

(the subscripts  $e$  and  $h$  stand for electrons and holes, respectively).<sup>3</sup>

$$I(h\nu) \sim \int_0^\infty f_e(E) D_e(E) f_h(h\nu - E_G - E) \times D_h(h\nu - E_G - E) dE. \quad (8)$$

In the present case  $f_h(E)$  is the Fermi distribution function and, assuming a low density and thermalization of the electrons,  $f_e(E)$  can be described by a Boltzmann distribution. We assume parabolic bands. Including the energy dependence of the transition probability, which is neglected in Eq. (8), in the way introduced by Benoit à la Guillaume and Cernogora,<sup>2</sup> and applying a Gaussian broadening that accounts for band-tailing effects, incomplete thermalization of the electrons, and the finite resolution in the experiment,<sup>18</sup> the following expression is obtained:

$$\bar{I}(h\nu) \sim \int_0^\infty I(h\nu') (h\nu' - E_0 - E_F)^{-2} e^{-[(h\nu' - h\nu)/E_s]^2} dh\nu' \quad (9)$$

with  $E_0$  as the direct-band-gap energy ( $\Gamma_c \rightarrow \Gamma_v$ ; see Fig. 1) and  $E_s$  as a broadening parameter.

Figure 3 displays a calculated luminescence spectrum, which has been fitted to the PL spectrum of the Ge:Ga

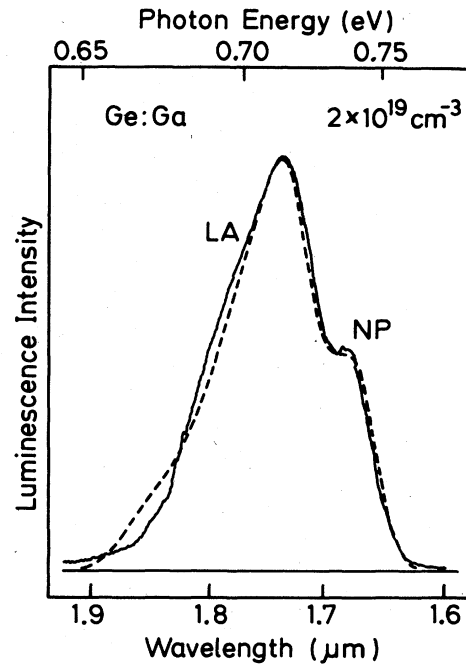


FIG. 3. Experimental spectrum of the indirect luminescence (solid curve) and calculated emission line shape (dashed curve). The fitting parameters are given in the text.

sample containing  $2 \times 10^{19}$  holes/cm<sup>3</sup>. To account for the overlapping NP and LA replicas in the experimental spectrum, two calculated curves were superimposed with a relative displacement equal to the LA phonon energy. The parameters obtained from the fit are  $E_F = 65$  meV,  $T = 25$  K, and  $E_s = 12$  meV. The intensity ratio between the NP and the LA phonon-assisted recombination was found to be  $I_{NP}/I_{LA} = 0.6$ . The band filling  $E_F$  deduced from the line-shape analysis compares reasonably well to the value of 73 meV calculated for  $2 \times 10^{19}$  holes/cm<sup>3</sup> using the hole density-of-states mass of pure germanium. The temperature of electrons and holes (25 K), obtained from the fit, is higher than the temperature of the exchange gas (5 K) due to the heating of the sample by the exciting cw laser beam (power density approximately equals 200 W/cm<sup>2</sup>). The agreement between the measured and the calculated spectrum is reasonably good except for the low-energy edge. But this discrepancy is most probably due to the crude model used in Eq. (9) to account for band-tailing effects.

In Fig. 4 the band-gap energy  $E_G$  and the energy of the optical gap ( $E_G + E_F$ ) as deduced from the PL spectra are shown as a function of the hole concentration  $N_h$ . Figure 4 also displays theoretical curves (see Sec. III) for  $E_G$  and  $E_G + E_F$  versus  $N_h$ . The  $E_G + E_F$  curve is obtained by adding the calculated band filling to the theoretical values for  $E_G$ . For the calculation of the band filling, the hole density-of-states mass of pure germanium of  $0.353m_0$  (Ref. 17) was used. The agreement between the experimental and the calculated values of  $E_G + E_F$  is reasonably good. The reduction of  $E_G$  with increasing hole concentration found experimentally, however, is smaller than the calculated gap shrinkage. Nevertheless we should keep in

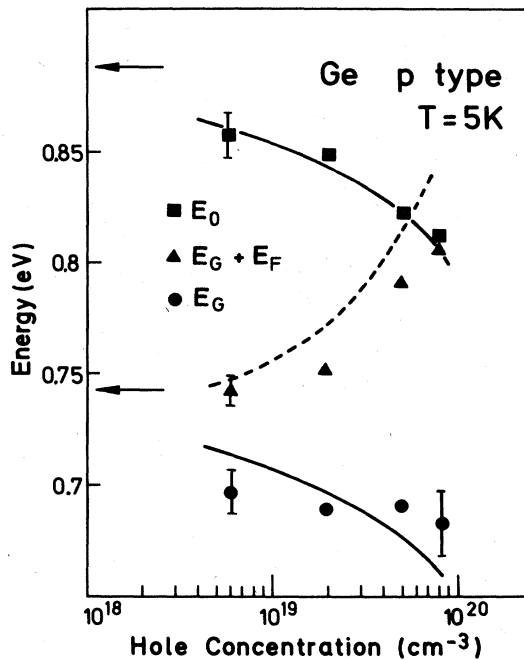


FIG. 4. Shift of the direct band gap  $E_0$ , of the indirect gap  $E_G$ , and of the optical gap  $E_G + E_F$  versus hole concentration. The drawn curves show the calculated shrinkage of  $E_0$  and  $E_G$ ; the dashed line indicates the calculated shift of  $E_G + E_F$  (see Sec. III). The arrows on the vertical scale show the gap energies  $E_0$  and  $E_G$  in pure Ge. Error bars for the experimental data are indicated.

mind that for increasing hole concentration the low-energy edge of the PL band becomes more and more smeared out and the overall luminescence intensity decreases, and therefore the experimental values of  $E_G$  become less accurate for larger hole concentrations.

### B. Direct luminescence

Besides the indirect recombination radiation at  $\approx 1.7 \mu\text{m}$ , we observe a luminescence peak at  $\approx 1.4 \mu\text{m}$ , which is due to radiative recombination across the gap  $E_0$  ( $\Gamma_c \rightarrow \Gamma_v$ ; see Fig. 1). Typical PL spectra are shown in Fig. 5 for three different hole concentrations. All three spectra were taken under identical experimental conditions such as excitation power density. The indirect luminescence band is strongly distorted due to the cutoff in sensitivity of the Ge diode at  $1.75 \mu\text{m}$ . Therefore the emission line shape and the relative intensities of the two replicas are altered compared to Fig. 2. With increasing hole concentration the direct-luminescence peak broadens and its low-energy edge shifts to lower energies.

Luminescence from the recombination across the gap  $E_0$  was reported earlier for pure germanium under intense optical excitation.<sup>8-10</sup> In this case the direct luminescence is due to the recombination of photocreated, non-thermalized electrons with photocreated holes. In our case, however, the holes are present because of the doping of the material and the number of additional holes created by the optical excitation is negligible. This difference

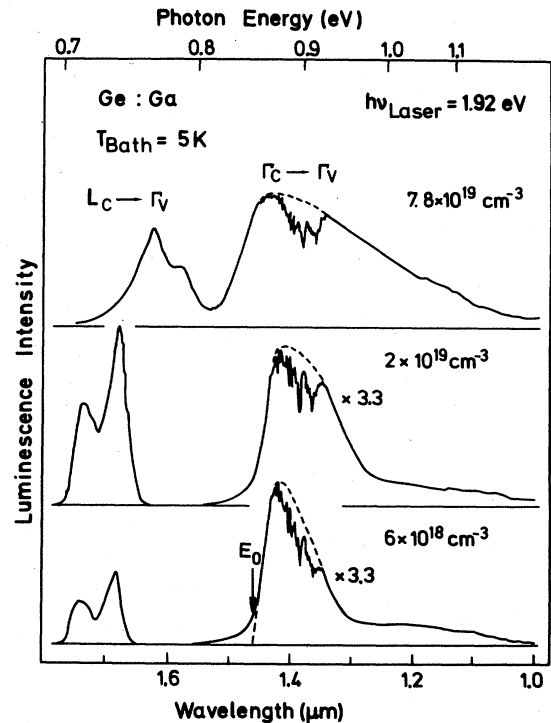


FIG. 5. PL spectra of *p*-type Ge for various hole concentrations, showing indirect ( $L_c \rightarrow \Gamma_v$ ) luminescence and direct ( $\Gamma_c \rightarrow \Gamma_v$ ) gap- $E_0$  emission. The spectra were recorded using a Ge photodiode. The indirect luminescence is distorted by the cutoff in detector sensitivity at  $1.75 \mu\text{m}$ . The sharp structure at  $\approx 1.4 \mu\text{m}$  is caused by atmospheric water absorption. Spectral resolution was  $24 \text{ \AA}$ .

manifests itself in the properties of the direct-luminescence band in two ways. First, in heavily doped *p*-type material the width and shape of the luminescence peaks varies with the dopant concentration (see Fig. 5), whereas for pure samples the shape of the direct peak only depends on the excitation power density.<sup>9,10</sup> Second, in pure material a power density of the order of  $1 \text{ kW/cm}^2$  is required to observe direct emission,<sup>10</sup> whereas in the doped samples used in the present study an excitation density of  $\approx 1 \text{ W/cm}^2$  was sufficient to detect emission across the gap  $E_0$ . The dependence on excitation power density is shown in detail in Fig. 6. For the direct as well as for the indirect luminescence in heavily doped *p*-type material a linear dependence of the luminescence intensity on the incident laser power is observed. This is reasonable because an increase of the incident power density only increases the number of electrons (minority carriers). The number of holes (majority carriers), however, is unaffected by the optical excitation, because the concentration of majority carriers is much larger than the concentration of photocreated electron-hole pairs. The intensity of the direct emission in pure germanium, in contrast, shows in our experiment a much stronger dependence with an exponent of  $3.5$ .<sup>19</sup> Both experiments on pure as well as on heavily doped samples were performed under the same experimental conditions.

Another point of interest is the dependence of the

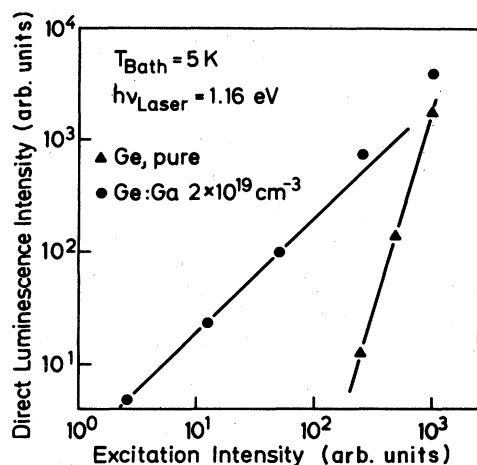


FIG. 6. Intensity of the direct luminescence versus excitation intensity for heavily doped *p*-type and, for reference, for pure Ge. Excitation intensity of  $10^3$  corresponds to an exciting power density of  $400 \text{ W/cm}^2$ .

direct-luminescence spectra on the exciting laser photon energy. Figure 7 displays PL spectra of Ge:Ga containing  $2 \times 10^{19}$  holes/cm<sup>3</sup> for three different exciting photon energies. Changing from 1.92- to 1.16-eV excitation, the direct-emission intensity increases by more than one order of magnitude compared to the indirect luminescence strength. Decreasing the exciting photon energy to 0.94 eV results in a further increase in the direct-emission intensity, but also the shape of the luminescence band changes. The peak becomes narrower; the low-energy edge remains unchanged whereas the high-energy tail shifts to lower energies.

The ratio of the direct- to indirect-luminescence peak intensity is shown in Fig. 8 versus exciting photon energy. Varying from 2.4- to 0.94-eV excitation, an increase of the relative strength of the direct emission by nearly three orders of magnitude is observed. The resonant behavior can be understood in terms of a strong dependence of the  $\Gamma_c$  to  $L_c$  scattering probability on the excess energy of the photoexcited electron. For exciting photon energies higher than the energy gap  $E_1$  of 2.2 eV, the excitation of an electron out of the valence band directly into the  $L$ -point conduction-band minima is possible, which leads to a strong-indirect and weak-direct emission. For exciting photon energies below the energy gap  $E_1$  on the other hand, electrons can only be excited into the conduction band  $\Gamma_c$ . For thermalization they have to scatter out of the  $\Gamma_c$  into the  $L_c$  minima. The minimum  $\vec{k}$  vector of the phonons required for such a scattering process increases with decreasing exciting photon energy and therefore the scattering probability decreases. This enhances the number of nonthermalized electrons "trapped" in the band  $\Gamma_c$  which leads to an increase of the direct emission compared to the indirect one with decreasing photon energy.

In order to understand the recombination mechanism for emission across the  $E_0$  gap, a detailed line-shape analysis was performed. For momentum-conserving tran-

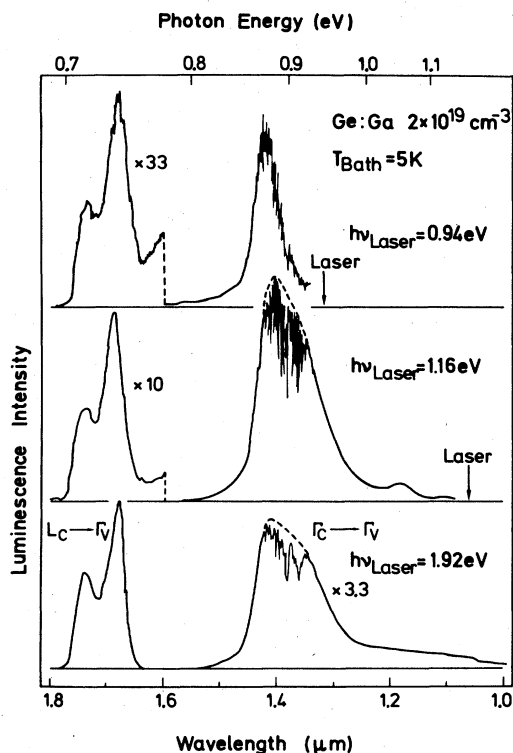


FIG. 7. PL spectra of *p*-type Ge containing  $2 \times 10^{19}$  holes/cm<sup>3</sup> for different exciting photon energies, showing indirect ( $L_c \rightarrow \Gamma_v$ ) and direct ( $\Gamma_c \rightarrow \Gamma_v$ ) emission. Note the change of the relative intensities and of the direct-luminescence line shape with varying exciting photon energy. The structure at  $\approx 1.4 \mu\text{m}$  is caused by atmospheric water absorption. Spectral resolution was  $24 \text{ \AA}$  for the lowest spectrum and  $8 \text{ \AA}$  for the upper spectra. The indirect luminescence is distorted by the cut-off in detector sensitivity at  $1.75 \mu\text{m}$ .

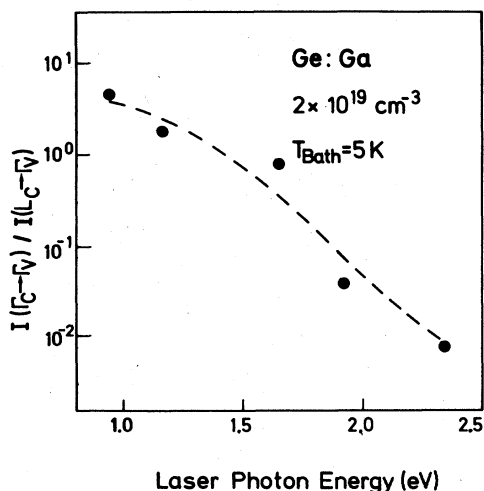


FIG. 8. Intensity ratio (corrected for Ge-detector response) of direct to indirect emission versus exciting photon energy. The dashed curve is drawn as a visual aid.

sitions, as one would expect for direct-gap recombination, the spectral shape of the luminescence band can be expressed as<sup>20</sup>

$$I(h\nu) \sim (h\nu - E_0)^{1/2} \left[ 1 + \exp \left[ a \frac{h\nu - E_0 - E_{Fe}}{k_B T_e} \right] \right]^{-1} \\ \times \left[ 1 + \exp \left[ b \frac{h\nu - E_0 - E_{Fh}}{k_B T_h} \right] \right]^{-1}, \quad (10)$$

with  $a = m_h / (m_e + m_h)$  and  $b = m_e / (m_e + m_h)$ ,  $T_e$  and  $T_h$  the temperature, and  $E_{Fe}$  and  $E_{Fh}$  the quasi-Fermi level of the electrons and the holes, respectively.  $m_h$  denotes the mass of the heavy-hole valence band and  $m_e$  the electron mass at the  $\Gamma_c$  conduction band minimum. The light-hole band will be neglected because of the smallness of the light-hole density-of-states mass.<sup>17</sup> In the present case, the electrons in the conduction band  $\Gamma_c$  are nonthermalized and their density is only small. Therefore the electron distribution function was approximated by a Boltzmann distribution with an "electron temperature" larger than the lattice or hole temperature<sup>21</sup> using the "hot electron" concept of transport theory.<sup>22</sup> In addition, the calculated line shape was convoluted with a Gaussian [see Eq. (9)] to account for band-tailing and lifetime-broadening effects. A distortion of the emission spectrum due to reabsorption was neglected for two reasons. First, the spectral variation of the absorption coefficient for photon energies slightly higher than the energy gap  $E_0$  is relatively small.<sup>23</sup> Second, the penetration depth of the exciting light ( $1 \mu\text{m}$  at  $1.16 \text{ eV}$ ) is smaller than the absorption length of the emitted luminescence [ $\approx 2 \mu\text{m}$  (Ref. 23)] and the diffusion length of the nonthermalized electrons in the band  $\Gamma_c$  can be assumed to be very small because of the small lifetime<sup>10</sup> and the low mobility in this heavily doped material.<sup>24</sup> Therefore, little influence of reabsorption on the direct luminescence is expected.

Figure 9 displays a spectrum of the direct luminescence recorded with high spectral resolution to minimize the effect of the sharp atmospheric water absorption lines around  $1.4 \mu\text{m}$  on the emission line shape. To fit the experimental direct emission spectrum, a combination of both wave-vector-conserving transitions as described by Eq. (10) as well as transitions *without* momentum conservations [see Eqs. (8) and (9)] was necessary. The breakdown of momentum conservation can be attributed to the scattering of the carriers among themselves and to carrier scattering by ionized acceptors.<sup>25</sup> Such a calculated line shape is also shown in Fig. 9. The parameters used were  $E_{Fh} = 65 \text{ meV}$  and  $T_h = 25 \text{ K}$ , as obtained from the fit of the indirect luminescence, and  $T_e = 250 \text{ K}$ . The broadening parameter used was  $E_s = 20 \text{ meV}$  and the ratio between momentum-conserving and momentum-nonconserving transitions was 3.0. The high "electron temperature" reflects, as discussed above, the nonthermalized distribution of the electrons in the minimum  $\Gamma_c$ .

A similar combination of direct transitions with and without momentum conservation has been observed in heavily doped *p*-type GaAs for the recombination across the gap  $E_0$ .<sup>25</sup> There an intensity ratio between transitions with and without momentum conservation of 3.3 and a

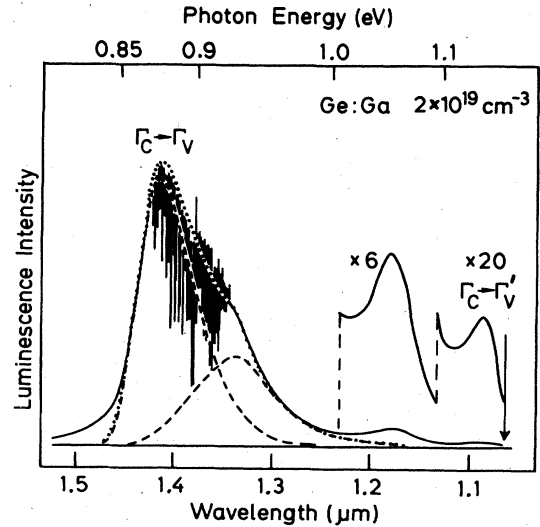


FIG. 9. PL spectrum (drawn line) showing emission across the gap  $E_0$  ( $\Gamma_c \rightarrow \Gamma_v$ ) and the gap  $E_0 + \Delta_0$  ( $\Gamma_c \rightarrow \Gamma'_v$ ). The arrow on the horizontal scale indicates the laser photon energy of  $1.16 \text{ eV}$ . The sharp structure at  $\approx 1.4 \mu\text{m}$  is caused by atmospheric water absorption. The spectral resolution was  $3.2 \text{ \AA}$ . Also shown is the fitted line shape (dotted curve), containing contributions with (dashed curve with maximum at lower energies) and without (dashed curve with maximum at higher energies) momentum conservation. The fitting parameters are given in the text.

broadening of  $35 \text{ meV}$  was found for a sample containing  $4 \times 10^{19} \text{ holes/cm}^3$ . The agreement between the data obtained for *p*-type GaAs and the data found in the present study for *p*-type Ge is surprisingly good, keeping in mind that in GaAs the gap  $E_0$  is the lowest one and therefore the minority carriers participating in the recombination across the gap  $E_0$  are thermalized, in contrast to the present case.

The shift of the gap  $E_0$ , as determined from the direct-luminescence spectra, is plotted in Fig. 4 as a function of the hole concentration. A comparison with the theoretical results (see Sec. III) shows a very good agreement between the calculated and the experimentally observed shift.

At the high-energy tail of the direct luminescence, two additional structures appear at  $1.049$  and  $1.141 \text{ eV}$  under  $1.16\text{-eV}$  excitation (both values refer to a hole concentration of  $2 \times 10^{19} \text{ cm}^{-3}$ ; see Fig. 9). For excitation with circularly polarized light, the angular momentum of the emitted photon at  $1.141 \text{ eV}$  has the same direction as the angular momentum of the absorbed photon, whereas for the photons emitted at  $1.049 \text{ eV}$  the direction of the angular momentum is reversed compared to that of the absorbed light.

The  $1.141 \text{ eV}$  peak is assigned to recombination across the gap  $E_0 + \Delta_0$  ( $\Gamma_c \rightarrow \Gamma'_v$  in Fig. 1), where both the electrons and the holes are photocreated. This assignment is based on the spectral position, which is  $290 \text{ meV}$  above the low-energy cutoff of the gap- $E_0$  emission. The shift of this peak as a function of the hole concentration is, within the experimental error, equal to the shift of the gap  $E_0$ , indicating a constant spin-orbit splitting  $\Delta_0$  indepen-

dent of the doping level.

The luminescence peak at 1.049 eV can be assigned to the excitation of an electron out of the light-hole valence band into the direct-conduction-band minimum immediately followed by the radiative recombination of this electron with a heavy hole. Between absorption and emission no relaxation of the electron within the conduction band is assumed. Such a process with  $k$  conservation is possible for a momentum of the photoexcited electron smaller than the Fermi momentum, as is the case for 1.16-eV excitation. Estimating the recombination photon energy for such a process we obtain 1.051 eV, in excellent agreement with the experimental peak position. Thereby we used an  $E_0$  gap energy of 0.85 eV, as determined from the direct luminescence (see Fig. 4), and the valence-band structure calculated by Kane.<sup>26</sup> Our interpretation is also consistent with the observed polarization properties. Dymnikov *et al.*<sup>27</sup> showed that, in agreement with our finding, for excitation of an electron out of the light hole band with circular polarized light, the recombination of this electron with a heavy hole gives rise to an emission of photons with the direction of the angular momentum reversed compared to the absorbed photons.

## V. CONCLUSIONS

We have studied in heavily doped  $p$ -type Ge the influence of hole concentration on the radiative recombination across the indirect fundamental gap and the direct band gap  $E_0$ . From the luminescence spectra the shrinkage of both band gaps was determined and compared to the results of full pseudopotential band-structure calculations. The emission across the gap  $E_0$  is found to resonate strongly for exciting photon energies close to the energy gap  $E_0$ . The line shape was calculated assuming a combination of transitions with and without momentum conservation. Despite the fact that the recombining electrons are not thermalized, the properties of the recombination across the gap  $E_0$  in  $p$ -type germanium are very similar to the ones of the emission across the fundamental gap in  $p$ -type GaAs.

## ACKNOWLEDGMENTS

We would like to thank M. Cardona and P. B. Allen for many helpful and stimulating discussions, and H. Hirt, M. Siemers, and P. Wurster for valuable experimental assistance.

<sup>1</sup>R. A. Abram, G. J. Rees, and B. L. H. Wilson, *Adv. Phys.* **27**, 799 (1978).

<sup>2</sup>C. Benoit à la Guillaume and J. Cernogora, *Phys. Status Solidi* **35**, 599 (1968).

<sup>3</sup>R. R. Parsons, *Solid State Commun.* **29**, 763 (1979).

<sup>4</sup>R. Rentzsch and I. S. Shlimak, *Phys. Status Solidi A* **43**, 231 (1977).

<sup>5</sup>A. Nakamura, *J. Phys. Soc. Jpn.* **43**, 529 (1977).

<sup>6</sup>J. Wagner, A. Compaan, and A. Axmann, *J. Phys. (Paris) Colloq.* **44**, C5-61 (1983).

<sup>7</sup>G. Contreras, A. Compaan, J. Wagner, M. Cardona, and A. Axmann, *J. Phys. (Paris) Colloq.* **44**, C5-55 (1983).

<sup>8</sup>J. R. Haynes and N. G. Nilsson, in *Proceedings of the 7th International Conference on the Physics of Semiconductors, Paris, 1964*, edited by M. Hulin (Dunod, Paris, 1964), p. 21.

<sup>9</sup>H. M. van Driel, A. Elci, J. S. Bessey, and M. O. Scully, *Solid State Commun.* **20**, 837 (1976).

<sup>10</sup>W. Klingenstein and H. Schweizer, *Solid State Electron.* **21**, 1371 (1978).

<sup>11</sup>P. B. Allen, *Phys. Rev. B* **18**, 5217 (1978).

<sup>12</sup>S. Doniach and E. H. Sandheimer, *Green's Functions for Solid State Physicists* (Benjamin, Reading, 1974).

<sup>13</sup>L. Viña and M. Cardona, *Phys. Rev. B* **29**, 6739 (1984).

<sup>14</sup>M. L. Cohen and T. K. Bergstresser, *Phys. Rev.* **141**, 789 (1966).

<sup>15</sup>J. A. Sanjurjo, E. López-Cruz, P. Vogl, and M. Cardona, *Phys. Rev. B* **28**, 4579 (1983).

<sup>16</sup>G. Lehmann and M. Taut, *Phys. Status Solidi B* **54**, 469 (1972); **57**, 815 (1973); J. Roth and A. J. Freeman, *Phys. Rev. B* **11**, 2109 (1975); O. Jepsen and O. K. Andersen, *Solid State Commun.* **9**, 1763 (1971).

<sup>17</sup>W. F. Brinkman and T. M. Rice, *Phys. Rev. B* **7**, 1508 (1973).

<sup>18</sup>W. P. Dumke, *Appl. Phys. Lett.* **42**, 196 (1983).

<sup>19</sup>It is interesting to note that the exponent of 3.5 found here with cw excitation at power densities of 100–400 W/cm<sup>2</sup> is about twice as large as the exponent of 1.6 reported in Ref. 10 for pulsed excitation and power densities of 0.8–6.7 kW/cm<sup>2</sup>.

<sup>20</sup>C. H. Gooch, *GaAs Lasers* (Wiley, London, 1969), p. 37.

<sup>21</sup>W. Klingenstein, Ph.D. thesis, University of Stuttgart, 1980.

<sup>22</sup>See, for example, K. Seeger, *Semiconductor Physics* (Springer, New York, 1973), p. 118.

<sup>23</sup>W. C. Dash and R. Newman, *Phys. Rev.* **99**, 1151 (1955).

<sup>24</sup>V. I. Fistul, *Heavily Doped Semiconductors* (Plenum, New York, 1969), p. 137.

<sup>25</sup>D. Olego and M. Cardona, *Phys. Rev. B* **22**, 886 (1980).

<sup>26</sup>E. O. Kane, *J. Phys. Chem. Solids* **1**, 82 (1956).

<sup>27</sup>V. D. Dymnikov, M. I. D'yakonov, and N. I. Perel', *Zh. Eksp. Teor. Fiz.* **71**, 2373 (1976) [*Sov. Phys.—JETP* **44**, 1525 (1976)].