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Recombination of donor bound-excitons in germanium

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The decay of the luminescence intensity associated with the LA-phonon-assisted recombination of free excitons in germanium is measured for samples with different donor concentrations. Simultaneously, the decay of the luminescence intensity originating from recombination of donor bound excitons is investigated. All measurements are carried out at temperatures where condensation into electron-hole droplets cannot be expected, i.e., above the critical temperature of 6.54 K. To exclude influences of electron-hole plasma the excitation power was also chosen low. The dependence of the experimental lifetimes on the arsenic donor concentration, as well as on the temperature, can be described by a system of equations including capture of free electrons into bound excitons and thermal dissociation of bound excitons into free excitons. The bound-exciton lifetime is determined to be 1.25 μsec in the As-donor case. Comparison of the experimental value to theoretical estimates of the exciton lifetimes leads to the conclusion that phonon-assisted Auger recombination must be a very effective channel for donor-bound-exciton decay.

INTRODUCTION

A lot of work has been published concerning electron-hole droplets (EHD) in germanium.[1] In particular, the transients of the EHD and free-exciton (FE) luminescence of pure and doped germanium have been investigated by Chen *et al.*[2-4] They observed a strong coupling between FE and EHD decay.

Our experiments deal with the luminescence lines originating from the radiative recombination of free and donor bound-excitons (BE) in germanium without being influenced by electron-hole droplets or electron-hole plasma. In our experiments, the donor bound-exciton lifetime is determined to be 1.25 μsec in the arsenic-donor case. This short lifetime cannot be explained by phononless Auger recombination, which is responsible for the bound-exciton lifetimes in silicon.[5]

Measuring the decay of the luminescence intensity after pulsed excitation for the FE (LA) and BE (no phonon) lines we get information about the interaction between free and bound excitons and the dominating recombination mechanism for donor bound excitons. Similar investigations concerning the interaction between free- and bound-exciton decay in silicon will be reported in a forthcoming paper by Silver.[6]

EXPERIMENT

Our samples have been germanium slices with approximate dimensions 5 × 5 × 1.2 mm and have been either of high purity ($n_D = 3.9 \times 10^9$ cm^{-3}, sample supplied by R. N. Hall) or As doped (in the range $n_D = 10^{15}$ cm^{-3}). They were polished and etched in a HF + HNO_3 solution before mounting. A typical luminescence spectrum of a doped sample is shown in Fig. 1. At a bath temperature of 4.2 K and high spectral resolution (0.2 meV), we observe besides the luminescence connected with electron-hole droplets [EHD (TO), EHD (LA), EHD (TA)], the radiation of the LA-assisted free-exciton recombination. Furthermore, the bound-exciton recombination accompanied by phonon emission can be seen as a small peak between the EHD (LA) and FE (LA) luminescence lines. The strong phononless radiative recombination line of the As-bound excitons appears at an energy near 739 meV. In order to avoid influence of electron-hole droplets on the decay kinetics, the bath temperature is raised to values above the critical temperature where condensation into EHD is not expected. The critical temperature in the case of germanium is 6.54 K. At those temperatures and low excitation power, only luminescence originating from excitonic recombination is observable. The corresponding spectrum is shown in the upper part of Fig. 1. To get high temporal resolution, we used a Ge photodiode with a time constant of only 5 nsec. Whereas for the lower part of the spectrum a PbS detector was used. Since the detectivity of the fast Ge photodiode was lower than the detectivity of the PbS detector, the spectral resolution (2 meV) had to be reduced.

The time resolution is limited due to the boxcar gate width and reaches a value of 150 nsec for the complete setup. The light for the excitation of electron-hole pairs is provided by a YAlG:Nd laser system (λ = 1.06 μm) with the laser beam defocussed to a spot of 5-mm diameter. The repetition frequency of the *Q*-switched system lies near 5 kHz.

RESULTS AND DISCUSSION

In Fig. 2 the luminescence intensity of the FE (LA) line measured in four different samples with donor concentrations between 3.9×10^9 and 4.3×10^{15} cm^{-3} is plotted in a logarithmic scale versus

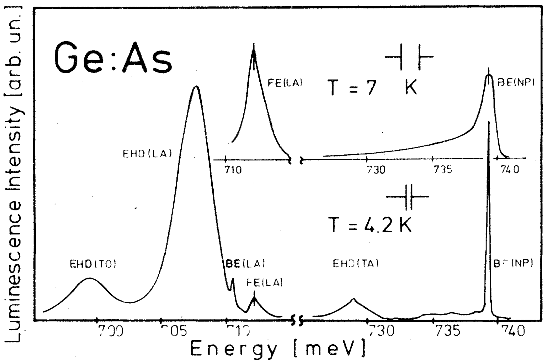

FIG. 1. Emission spectra of the phononless and phonon-assisted radiative recombination at the indirect gap of As-doped ($10^{15}\mathrm{cm}^{-3}$) germanium. Lower part: Excitonic and droplet emission lines taken at a bath temperature of 4.2 K and high (0.2 meV) spectral resolution. Upper part: Free- and bound-exciton luminescence taken at a bath temperature of 7 K. The spectral resolution (2 meV) is reduced due to the detector sensitivity of the Ge photodiode used in time-resolved measurements.

time. The decay is exponential in the whole time regime investigated. For the high-purity sample we get a time constant of 4.56 μsec for the decay. This value is somewhat lower than values given by Pokrovskii[7] (8 μsec), Chen *et al.*[3] (6–7 μsec) and very close to a value of 5 μsec used by Thomas *et al.*[8] in their calculations. With increasing donor concentration the lifetime of the free excitons shortens. The experimental values are given in Fig. 2 and reach 1.2 μsec for a concentration of 4.3×10^{15} cm^{-3} arsenic donors in the crystal. The faster decay of the free-excitons in the presence of donor impurities demonstrates that the recombination of free-excitons is determined by the capture of excitons at impurities and subsequent decay as bound-excitons.

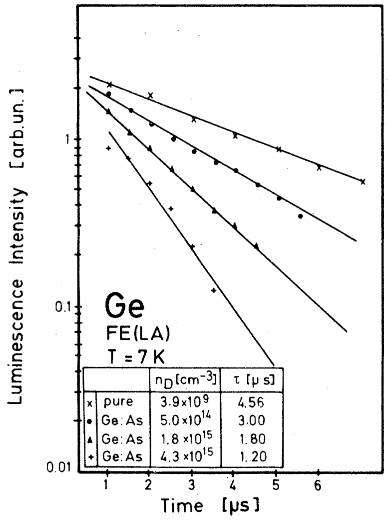

FIG. 2. Luminescence intensity of the free-exciton radiative recombination accompanied by the emission of a LA phonon is plotted vs time on a logarithmic scale. The decay is exponential and the different slopes correspond to different impurity concentrations as indicated in the figure. Further details are given in the text.

Therefore, we propose the following kinetic equations to describe the coupled decay of free and bound excitons in germanium: The time derivative of the free-exciton concentration is given by

$$\frac{dn_{\mathrm{FE}}}{dt}=-\frac{n_{\mathrm{FE}}}{\tau_{\mathrm{FE}}}-n_{\mathrm{FE}}(n_D-n_{\mathrm{BE}})\sigma v_{\mathrm{th}}+An_{\mathrm{BE}}\,, \qquad (1)$$

that is the sum of recombination of free excitons, the capture of free-excitons under formation of bound-excitons, and finally the thermal dissociation of bound-excitons into free excitons. All possible recombination channels without participation of donors are enclosed in the lifetime τ_{FE}. Especially, this lifetime includes nonradiative recombination channels. The radiative lifetime for free excitons has a value near 500 μsec using results of Bênoit à la Guillaume *et al.*[9] and Leheny *et al.*[10] The donor concentration is denoted by n_D and all donors are assumed to be neutral at those temperatures. Finally, the capture cross section for the capture of free-excitons is denoted by σ and the thermal velocity of the free-excitons by v_{th}.

Consequently, the time derivative of the bound-exciton concentration is given by

$$\frac{dn_{\mathrm{BE}}}{dt}=-\frac{n_{\mathrm{BE}}}{\tau_{\mathrm{BE}}}+n_{\mathrm{FE}}(n_D-n_{\mathrm{BE}})\sigma v_{\mathrm{th}}-An_{\mathrm{BE}}\,, \qquad (2)$$

i.e., the recombination of donor bound-excitons with a characteristic time constant τ_{BE}, the capture of free excitons and the thermal activation of bound excitons into free-excitons. Again, the capture cross section is denoted by σ, the thermal velocity of the excitons by v_{th}. The difference n_D-n_{BE} takes into account possible saturation effects, i.e., all neutral donor impurities should bind only one exciton forming a D^0X complex.

The constant describing thermal dissociation of bound-excitons into free-excitons

$$A=g\sigma v_{\mathrm{th}}(2\pi m^*kT/h^2)^{3/2}\exp(-E/kT) \qquad (3)$$

is proportional to the degeneracy factor g, the capture cross section σ, the thermal velocity v_{th}, an effective density of states and a Boltzmann factor containing the localization energy E of the exciton in a D^0X complex. For our calculations we take a value of $E=1{:}33$ meV (see Ref. 11) for the arsenic donor.

Comparison of the different terms involved in Eqs. (1) and (2) leads to the conclusion, that the temperature dependence of the decay of the free-excitons in doped samples is mainly determined by the thermal dissociation constant A, whereas the variation of the lifetime with donor concentration is determined by the capture probability σv_{th}. Therefore, the parameter A can be obtained from a fit of the temperature dependence of the free-exciton lifetime keeping the donor concentration constant. In addition, it is possible to obtain the capture probability σv_{th} by fitting the dependence of the free-exciton decay time constant on donor concentration at constant temperature. The lifetime τ_{FE} of free-excitons for recombination without participation of donors can be taken either from measurements using high-purity germanium or from the decay kinetics of doped samples in the high-temperature limit. In both cases, the interaction with the donors are thought to be negligible. Thus, the only remaining parameter to fit the bound-exciton decay curves is the bound-exciton lifetime, which can be extracted from the experiments in this way.

In Fig. 3, the theoretical and experimental time behavior of the luminescence intensities for free- and bound-exciton recombination are shown. For the decay behavior shown in this figure, the temperature is kept constant and the net donor concentration is varied. The absolute values for the exciton densities are calculated by Eqs. (1) and (2) adding a generation rate g to Eq. (1). This generation rate g is given by the incident laser power. Since exact values of the external radiative quantum efficiency for free- and bound-exciton recombination are not known and might even differ from sample to sample because of surface effects, it is impossible to get the absolute free- and bound-exciton concentrations from luminescence experiments directly. However, the exact numerical values are not necessary for the quantitative evaluation of the data. The experimentally observed luminescence intensities are, therefore, normalized to the theoretical values of the densities.

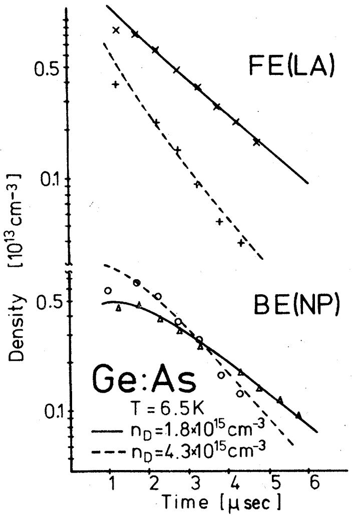

FIG. 3. Time decay of the free- and bound-excitons is drawn for two different donor concentrations. Upper part: Free-exciton luminescence. The solid and dashed lines are calculated as described in the text. The time constants are 1.8 μsec for a donor concentration of 1.8 $\times10^{15}$ cm^{-3} and 1.2 μsec for a donor concentration of 4.3 $\times10^{15}$ cm^{-3}. Lower part: Corresponding bound-exciton luminescence. The decay can be described by a time constant of 2.5 μsec for the lower and 1.6 μsec for the higher doping level. Further details are given in the text.

In the upper part, the time decay of the free-exciton luminescence is shown. The solid line corresponds to a germanium sample with an As doping level of 1.8×10^{15} cm^{-3}. The experimental points are marked by crosses and yield a time constant of 1.8 μsec. The dashed line corresponds to an As donor concentration of 4.3×10^{15} cm^{-3} and the experimental luminescence intensities are marked by plus signs. The decay time constant is 1.2 μsec for the free-excitons.

In the lower part, the time decay of the bound-exciton luminescence is shown. Again the solid line corresponds to the lower and the dashed line to the higher doping level as indicated in the figure. The respective experimental values for the bound-exciton decay are marked by triangles and circles. The decay can be described approximately by a time constant of 2.5 μsec for the lower doping level and 1.6 μsec for the higher doping level. The decay is not really exponential which can be verified easily regarding the kinetic Eqs. (1) and (2). The exponential behavior of the free-exciton lines, in contrast, is a very good approximation because of the values of the capture and dissociation constants as well as the donor concentration used in the experiments. As described above, from this set of decay curves the bound-exciton lifetime can be extracted. The agreement between theoretically computed and experimentally observed decay curves is best for a lifetime τ_{BE} of the As-donor bound-excitons with a value of 1.25 μsec.

As mentioned above, the influence of bound excitons on the recombination of free-excitons is reduced with raising temperature. In Fig. 4, the luminescence intensities of the FE (LA) line are plotted versus time for different bath temperatures (curves 1 to 5) measured for a sample with a donor concentration of 4.3×10^{15} cm^{-3}. Again, the density scale denotes the calculated free-exciton concentration using a generation rate g added to Eq. (1). The experimental decay curves are normalized to these densities. When the bath temperature is raised from 6.5 to 22 K, the decay

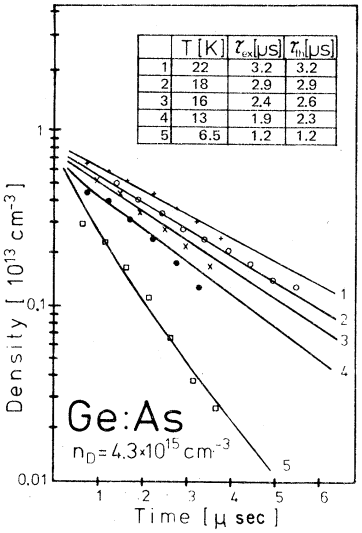

FIG. 4. Free-exciton luminescence is plotted vs time for different temperatures. The donor concentration is kept constant at 4.3×10^{15} cm^{-3}. The solid lines are calculated as described in the text. The insert gives a compilation of the different temperatures and the respective calculated and experimental decay time constants.

time constant for the FE (LA) line increases from 1.2 to 3.2 μsec. The decay time constants extracted from the experimentally observed and the calculated time behavior of the FE (LA) luminescence corresponding to different temperatures are compiled in the inset to Fig. 4. The agreement between experimental and theoretical decay time constants is very good and confirms our assumptions concerning the coupling between free- and bound-exciton decay expressed in Eqs. (1) and (2). Raising temperature, the thermal dissociation becomes more and more important and reduces the efficiency of the recombination of free-excitons via bound-excitons. Thus the decay time constant lengthens. The decay time constant for high-purity germanium turns out to be independent of temperature and remains at a value of 4.56 μsec, the free-exciton lifetime.

RECOMBINATION MECHANISMS

Our experiments yield a lifetime of 4.56 μsec for the free excitons, whereas the lifetime of bound excitons is 1.25 μsec in the case of the As donor. Therefore, in the case of the As donor impurity, the bound-exciton lifetime cannot be governed by the free-exciton lifetime as proposed by Osbourn and Smith[12] for acceptor bound-excitons. There must exist a separate and effective recombination channel for the bound excitons instead.

In Fig. 5, four possible recombination mechanisms for donor bound-excitons are depicted: (a) the phononless radiative recombination and (b) phonon-assisted radiative recombination; and (c) the phononless Auger recombination and (d) phonon-assisted Auger recombination. For each recombination mechanism a schematic band structure of germanium is given, showing the indirect *L* and direct Γ conduction band minima, as well as the nearly degenerate heavy- and light-hole valence bands and the split-off valence band. The corresponding transitions are marked by arrows. The energies $h\nu$ denote the emission of a photon and $\hbar\omega$ is the energy of the phonon involved.

In Fig. 5(a), the scheme of the phononless radiative recombination is shown. Considering the schematic band structure of germanium, there are in the case of neutral donor bound-excitons two electrons at the *L* minimum of the conduction band with a *k* vector $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and one hole at the Γ-

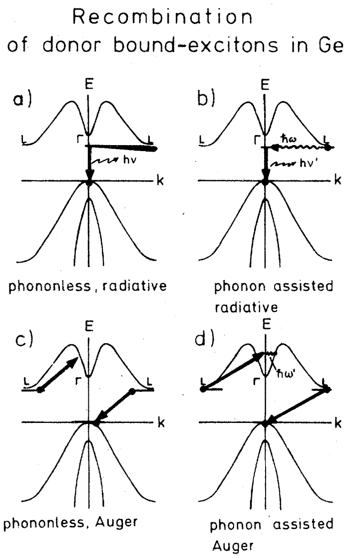

FIG. 5. Schematic diagram of four possible recombination mechanisms of donor-bound excitons in germanium. The transitions are denoted by arrows. The schematic band structure of germanium shows the direct Γ and indirect *L* conduction-band minima as well as the heavy- and light-hole valence bands (in this figure degenerate) and the split-off valence band. (a) Phononless radiative recombination: the electron wave functions are extended from the *L* to the Γ minimum. The emitted photon is marked by $h\nu$. (b) Phonon-assisted radiative recombination: The emitted phonon is denoted by $\hbar\omega$. (c) Phononless Auger recombination: The electron and hole wave functions have to be extended in *k* space to guarantee energy and momentum conservation. (d) Phonon-assisted Auger recombination: Energy and momentum conservation are guaranteed by an additional phonon. The spreading of the electron and hole wave functions is therefore not important in this case.

valence-band maximum with $\vec{k}=0$. Momentum conservation can be guaranteed by a transfer to the neutral impurity. In a quantum-mechanical picture, the wave functions of particles bound to an impurity are "smeared" in k space and, therefore, provide a certain probability for the electrons in the D^0X complex at $\vec{k}=0$. Using a semiclassical theory, as described by Dexter[13] for example, we get the following connection between the absorption and the radiative lifetime

$$\tau_{\text{rad}} = (\hbar^3 c^2 \pi^2 N/\epsilon E_m^2) \int \alpha(E)\, dE\,. \tag{4}$$

Taking absorption data from Ayrault's work,[14] we can estimate the integrated absorption for the arsenic donor in germanium to have the value

$$\int \alpha(E)\, dE = 2.9\times 10^{-5}\ \text{meV}\,\text{cm}^{-1}\,. \tag{5}$$

The absorption data are taken from a sample with a donor concentration of $N=1.8\times10^{16}\ \text{cm}^{-3}$. E_m denotes the peak position of the absorption line. The dielectric constant ϵ has a value of 15.36 for germanium.[1] Thus, Eqs. (4) and (5) finally yield a lifetime of 185 μsec for the phononless radiative recombination if we use the numerical values given above. The computed lifetime is about two orders of magnitude too long to explain our measured decay time constant of 1.25 μsec. Therefore, phononless radiative recombination is by far not effective enough to determine the lifetime of donor-bound excitons.

Next, the phonon-assisted radiative recombination is considered. For this process, the emission of a photon is accompanied by the simultaneous emission or absorption of a phonon to guarantee energy and momentum conservation. In the spectra, the emission lines are shifted by the phonon energy to higher or lower energies in comparison to the band-edge energy. If we consider the luminescence intensities of the BE (NP) and the BE (LA) lines, we find that the phonon-assisted emission is about a factor 5 to 10 less intensive than the phononless transition. This means that the lifetime for the phonon-assisted radiative recombination is at least a factor of 5 longer than in the phononless case. Therefore, lifetime of donor-bound excitons cannot be governed by phonon-assisted radiative processes.

One possible nonradiative process is the phononless Auger transition [Fig. 5(c)]. This process is characterized by the recombination of one electron with a hole and the simultaneous excitation of the second electron to a higher level in the conduction band. This Auger mechanism has been proposed by Dean *et al.*[15] to explain the recombination of acceptor bound excitons in GaP. Furthermore, this process has been discussed by Schmid[5,16] in explaining the recombination of D^0X and A^0X complexes in silicon. Osbourn and Smith,[12] as well as Osbourn *et al.*,[17] treated in their work Auger recombination predominantly of A^0X complexes in Si. Since the final states are defined by the band structure, in the case of germanium energy and momentum conservation can be accomplished only, when the bound electron and hole wave functions are spread in k space. In the case of donor-bound excitons, there are two electrons and one hole involved. Therefore, we have to consider *eeh* Auger processes only. Taking into account the spreading of the electron and hole wave functions and the band structure of germanium, this offers the possibility that one electron recombines with the hole, whereas the other electron is excited to a state near the direct Γ conduction band minimum.

To get a feeling for the time constants involved, we want to consider calculations of Osbourn and Smith[12] concerning the Auger transition rates of A^0X complexes in germanium. To calculate the lifetimes for different impurities, they use a square well potential appropriate for the impurities. For reasonable square well parameters they get lifetimes of 10^{-2} sec or longer in the case of germanium. Those long lifetimes, as calculated for the phononless Auger recombination in germanium in comparison to Si and GaP, are connected with the smaller binding energies and therefore larger Bohr radii[12] of the impurities in Ge compared to silicon or GaP. In the D^0X case no analogous calculations exist. The difference between the A^0X and the D^0X case is mainly due to the different final states of the excited Auger particles defined by the band structure. The band structure, that determines the final states, is expected to influence the Auger transition probabilities in the same way in the case of bound-excitons as in the case of band-to-band recombination. For the band-to-band Auger recombination, Huldt[18] has calculated the Auger coefficients for phononless *eeh* and *ehh* recombination processes. Although, at a first glance, the *eeh* process in germanium seems to be more probable than the *ehh* process because of the direct Γ conduction-band minimum and the small effective mass at this Γ minimum, Huldt[18] gets nearly equal probabilities for both processes. Depending on the exact numerical values used, the ratio of *eeh* to *ehh* Auger coefficients is in the range 0.1 to 0.5. If we assume that the probability ratio of D^0X and A^0X complexes is the same as in the *eeh* and *ehh* band-to-band Auger recombination, respectively, we can estimate the lifetime of the D^0X complex. In the acceptor case, Osbourn and Smith[12] calculated the Auger lifetime to be in the order of 10^{-2} sec, as mentioned above. Taking into account the probability ratio for the Auger recombination processes, the lifetime of D^0X complexes is expected to be at least 10^{-3} sec or longer. We conclude therefore, that the phononless Auger recombination of the donor bound-excitons in germanium cannot explain the experimentally observed lifetime of 1.25 μsec in the arsenic donor case.

For the small donor-binding energies in the case of germanium (14 meV for As) we expect the carriers in the D^0X complex to have more analogy to free particles than in the case of silicon (53.5 meV for As) or GaP. For free particles, the phonon-assisted Auger recombination is established to be the most effective recombination channel[19,20] in the case of germanium and silicon. A schematic diagram of such transitions is shown in Fig. 5(d). Again, one of the electrons recombines with the hole of the D^0X complex. The second electron at the same time is excited to a virtual state at $\vec{k}=0$ and finally the transition to a real band state under energy and momentum conservation is guaranteed by a phonon. Although, the phonon-assisted process is a second-order process, this transition might have a higher probability. The reason is that phonon participation avoids a spreading of the wave functions in k space to conserve momentum and the spreading is small in the case of small binding energies of the impurities. To get an estimate for the lifetime connected with phonon-assisted Auger recombination it is necessary to make some assumptions in the D^0X case. First, the carrier concentration for the D^0X complex is taken to be homogeneous within a sphere given by a radius near the Bohr radius of the donor, i.e.,

$$n = 1/\tfrac{4}{3}\pi a_d^3 \beta^3 . \qquad (6)$$

Here a_d denotes the neutral donor Bohr radius, given in cm as

$$a_d = (7.2\times10^{-9}/\epsilon E_B) , \qquad (7)$$

where E_B is the donor-binding energy in eV, and ϵ is the dielectric constant. In the D^0X case, the carriers are thought to be distributed within a sphere, that is enlarged by a factor $\beta > 1$ in comparison to the neutral donor case.

In the acceptor case, Pan *et al.*[21] calculated the ratio of dissociation energy to acceptor binding energy in dependence on the effective mass ratio. They used a simple set of trial wave functions:

$$\Psi_h \propto e^{-r_1/\alpha} e^{-r_2/\alpha} ;$$

$$\Psi_e \propto (1 + r_e/\beta + r_e^2/2\beta^2) e^{-r_e/\beta} . \qquad (8)$$

The radii are normalized to the Bohr radius. In their variational calculation, they found the electron wave function parameter β to vary between 1.3 and 4.25 and the hole wave-function parameter α to take values between 1.3 and 1.45 dependent on the effective mass ratio. On the other hand, Sharma and Rodriguez[22] calculated analogously the ratio of dissociation energy to donor-binding energy in dependence on the effective mass ratio in the D^0X case. They got a very similar result to Pan *et al.*[21] Therefore, we conclude, that the modification of the wave functions should be in the same order of magnitude in the D^0X and in the A^0X case. This leads to an upper limit of 4 and a lower limit of 1 for the parameter β in Eq. (6). Another approach to the parameter β can be done following the calculations of Munchy[23] concerning the binding energies of D^0X complexes. In a simplified picture, the D^0X complex can be thought to consist of two heavy positive centers, the ionized donor and the positive hole. These centers are bound together by the two electrons. Analogous to the H_2 molecule, the electron distribution is expected to be large mainly between the two positive charges. Therefore, we can estimate the spreading of the electron distribution by the distance of the two positive charges. The distance, in the case of an infinite hole mass, is 54 Å. The distance in the case of an electron-to-hole mass ratio of one is 62.2 Å. These values are computed following the calculation of Munchy[23] and using a dielectric constant of 15.36 for germanium.[1] The effective masses used in the calculation are 0.22 for the electron and 0.347 for the hole mass as given by Brinkman and Rice.[24] Interpolation between these two extreme distances using the effective masses given above, yields a value of 59 Å. Comparing this Bohr radius to the donor Bohr radius of the arsenic donor (33 Å) in germanium, the parameter β is determined to have a value of 1.8. Taking this parameter β and considering that two electrons are enclosed in that volume, we get a carrier concentration of 2.3×10^{18} cm^{-3} using Eq. (6).

The Auger coefficient for free-particle Auger recombination has been determined experimentally for example by Conradt and Aengenheister,[25] Auston and Shank[26] and Bénoît à la Guillaume *et al.*[27] to a value near 10^{-31} cm^6 sec^{-1}. Recent theoretical calculations of Haug[28] for different phonon-assisted Auger processes give detailed values near 10^{-31} cm^6 sec^{-1}, and 1.2×10^{-31} cm^6 sec^{-1} for the relevant *eeh* process, especially.

Taking the carrier concentration estimated above and the Auger coefficient given by Haug[28] we compute a lifetime (in μsec) of

$$\tau_{eeh} = 1/Cn^2 = 1.6 \qquad (9)$$

for the phonon-assisted Auger recombination of donor-bound excitons. The lifetime, deduced from our experiments has been 1.25 μsec. Taking into account the above-mentioned assumptions and the uncertainties in the determination of an exact carrier concentration, the agreement between the theoretically estimated and the experimentally observed value of the lifetime of As bound excitons in germanium is very good. This confirms that the short lifetime of donor-bound excitons can be explained by a phonon-assisted Auger process.

CONCLUSIONS

We have measured the lifetimes of free and bound excitons in germanium. In the case of free excitons we get a value of 4.56 μsec for the lifetime. In the case of donor-bound excitons, we measure a lifetime of 1.25 μsec for the arsenic donor. The decay of free and bound excitons is strongly coupled and can be described by a system of differential equations that take into account the capture of free excitons and the thermal ionization of bound excitons. All recombination processes without participation of bound excitons are comprised in a time constant τ_{FE}; all recombination processes of bound excitons except the thermal ionization are comprised in the lifetime τ_{BE} of bound excitons.

Consideration of phononless and phonon-assisted radiative recombination, as well as phononless and phonon-assisted Auger recombination, leads to the conclusion that phonon-assisted Auger recombination must be the process responsible for the short lifetimes. This is in contrast to the case of silicon, where the phononless Auger recombination is in good agreement to the observed time constants. This is caused by the small binding energies of impurities in germanium in comparison to silicon. Therefore, the phonon-assisted Auger process is the only one, that provides bound-exciton lifetimes in the microsecond range. The theoretically estimated value of 1.6 μsec for the As donor-bound excitons is in a very good agreement to the experimentally observed value of 1.25 μsec.

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[1] See, for example, J. C. Hensel, T. G. Phillips, G. A. Thomas, and T. M. Rice, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1977), Vol. 32.

[2] M. Chen, D. L. Smith, and T. C. McGill, Phys. Rev. B 15, 4983 (1977).

[3] M. Chen, S. A. Lyon, K. R. Elliott, D. L. Smith, and T. C. McGill, Nuovo Cimento B 39, 622 (1977).

[4] M. Chen, S. A. Lyon, D. L. Smith, and T. C. McGill, Phys. Rev. B 17, 4744 (1978).

[5] W. Schmid, Phys. Status Solidi B 84, 529 (1977).

[6] R. N. Silver, Phys. Rev. Lett. (to be published).

[7] Ya. E. Pokrovskii, Phys. Status Solidi A 11, 385 (1972).

[8] G. A. Thomas, A. Frova, J. C. Hensel, R. E. Miller, and P. A. Lee, Phys. Rev. B 13, 1692 (1976).

[9] C. Benoît à la Guillaume, M. Voos, and F. Salvan, Phys. Rev. B 5, 3079 (1972), B 7, 1723 (1973), and references therein.

[10] R. F. Leheny, J. Shah, and M. Voos, Solid State Commun. 20, 819 (1976).

[11] R. Martin, Ph.D. thesis (Universität Stuttgart, 1974) (unpublished).

[12] G. C. Osbourn and D. L. Smith, Phys. Rev. B 16, 5426 (1977).

[13] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 6.

[14] B. Ayrault, Thèse de doctorat d'état ès sciences physiques (Faculté des Sciences de Paris, 1970) (unpublished).

[15] P. J. Dean, R. A. Faulkner, S. Kimura, and M. Ilegems, Phys. Rev. B 4, 1926 (1971).

[16] W. Schmid, Solid State Electron. 21, 1285 (1978).

[17] G. C. Osbourn, S. A. Lyon, K. R. Elliott, D. L. Smith, and T. C. McGill, Solid State Electron. 21, 1339 (1978).

[18] L. Huldt, Phys. Status Solidi A 8, 173 (1971).

[19] W. Lochmann, Phys. Status Solidi A 45, 423 (1978).

[20] L. Huldt, Phys. Status Solidi A 33, 607 (1976).

[21] D. S. Pan, D. L. Smith, and T. C. McGill, Solid State Commun. 18, 1557 (1976).

[22] R. R. Sharma and S. Rodriguez, Phys. Rev. 159, 649 (1967).

[23] G. Munchy, J. Phys. (Paris) 28, 307 (1967).

[24] W. F. Brinkman and T. M. Rice, Phys. Rev. B 7, 1508 (1973).

[25] R. Conradt and J. Aengenheister, Solid State Commun. 10, 321 (1972).

[26] D. H. Auston, C. V. Shank, and P. LeFur, Phys. Rev. Lett. 35, 1022 (1975).

[27] C. Benoît à la Guillaume, M. Voos, and Y. Petroff, Phys. Rev. B 10, 4995 (1974).

[28] A. Haug, Solid State Commun. 25, 477 (1978).