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Radiative Recombination of Biexcitons in Germanium

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Photoluminescence of pure germanium excited in an electron-hole pair concentration range between 10^{12} and 10^{16} cm^{-3} is investigated at low temperatures from 2.0 to 4.2°K. The temperature and concentration dependences of two radiation lines with quantum energies 0.713 and 0.708 eV are measured. The first line is known to be due to free excitons; it is assumed that the second line is due to annihilation of exciton molecules (biexcitons). The experimental data pertaining to both surface and volume excitation can be consistently explained from the viewpoint of a biexciton nature of the 0.708 eV line. The dissociation energy of an exciton molecule in germanium is estimated to be 3.6–3.8 meV. An effect of nonequilibrium phonons (with an energy of the order of 1.6 meV and produced when the excitons are bound into biexcitons) on the ratio between the exciton and biexciton concentrations in the system under consideration is observed.

OBSERVATION of radiative recombination of biexcitons in silicon and germanium was reported in[1-7]. The main proof obtained in these papers for the existence of biexcitons reduces to the following. The intensity of the biexciton radiation depends quadratically on the intensity of the free-exciton radiation; second, the quadratic dependence is observed in a wide range of excitations, up to those at which the biexciton line becomes dominant in intensity[1)].

In the investigation of radiative recombination in germanium[2,3] it was observed that at high excitation levels the quadratic dependence gives way to a linear one. It was shown in[3,6] that the linear dependence is the consequence of accumulation in the sample of a large number of nonequilibrium phonons, which shift the quasiequilibrium in the exciton-biexciton system in the direction of production of free excitons.

On the other hand, the authors of a large number of recent papers cast doubt on the existence of biexcitons in silicon and germanium[9-13]. They assume that the radiation in question belongs in fact to the condensed state of the excitons, with density 2×10^{17} cm^{-3} for germanium and 5×10^{18} cm^{-3} for silicon. This density exceeds somewhat the values $|\psi(0)|^2$ expected for excitons in these substances. The existence of a condensed state with such a high density is paradoxical, since the indicated values of $|\psi(0)|^2$ are a result of attraction of unscreened electrons and holes, whereas the interaction between individual atoms in the condensed phase is always significantly screened. Observation of the condensed phase with a much lower density was reported in[14,15].

We present here the results of investigations undertaken for the purpose of obtaining additional data on the nature of the long-wave recombination radiation in germanium and determining the binding energy of biexcitons. Some preliminary results of this investigation were published earlier in[3,6,7].

I. INTRODUCTION

The energy and momentum conservation laws for the formation of a biexciton out of two excitons at rest, with emission of a phonon $\hbar\omega_f$, can be written in the form

$$\hbar\omega_f + \Delta E = E_b, \quad -\hbar k_b = \hbar\omega_f / s, \tag{1}$$

where ΔE is the "recoil" energy acquired by the biexciton when it emits a phonon, E_b is the dissociation energy of the exciton molecule, and s is the speed of sound. We shall show later that in germanium E_b amounts to several millielectron volts. Then the frequency of the emitted phonons turns out to be of the order of 10^{12} Hz. It is known that such phonons have very large lifetimes in pure semiconductors at low temperatures[16-18]. If the phonon lifetime exceeds the exciton and biexciton lifetimes, and the phonon concentration is high enough, then the behavior of the nonequilibrium electron-hole system turns out to be significantly different than in the absence of such phonons[3]. The kinetic equations for the excitons and biexcitons are[2,13]

$$\begin{aligned}\frac{dn_{ex}}{dt} &= J - \frac{n_{ex}}{\tau_{ex}} + \frac{n_b}{\tau_b} - 2\sigma v(n_f+1)n_{ex}^2 + 2\sigma v\gamma n_f n_b e^{-\Delta E/kT},\\ \frac{dn_b}{dt} &= -\frac{n_b}{\tau_b} + \sigma v n_{ex}^2(n_f+1) - \sigma v\gamma n_f n_b e^{-\Delta E/kT},\end{aligned} \tag{2}$$

Here n_f is the number of phonons in a given state, σ is the cross section for the binding of two excitons into a biexciton,

$$\gamma = \frac{g_{ex}^2}{g_b}\left(\frac{m_{ex}^*}{m_b^*}\right)^{3/2}\left(\frac{2\pi m_{ex}^* kT}{h^2}\right),$$

and g_{ex} and g_b are the degeneracy factors of the exciton and biexciton states. Pulsed excitation was used in this investigation, and the pulse duration Δt was always much shorter than the lifetime of the excitons and holes relative to their interband recombination. Therefore the concentration of the electron-hole pairs generated in the sample was determined in terms of the generation rate J, namely $N = J\Delta t$. If τ_{ex}

[1)] This last circumstance is quite important, since this is precisely what makes it possible to distinguish the recombination of the biexcitons from recombination on collision of two excitons[8], the intensity of which also depends quadratically on the exciton concentration. However, recombination on collision is a process described by a higher order of perturbation theory than recombination of free excitons and its intensity should consequently be much lower than the exciton intensity.

$\gg (\sigma\nu n_{ex})^{-1}$, then the system in question is in quasi-equilibrium, and it follows from (2) that

$$n_{ex}^2(n_f+1) = \gamma n_b n_f e^{-\Delta E/kT}. \tag{3}$$

At a low excitation level, when the nonequilibrium phonons can be neglected, $n_f = n_{f_0} \sim e^{-\hbar\omega t/kT}$, and we obtain

$$n_{ex} = \gamma^{1/2} n_b^{1/2} e^{-E_b\, 2kT}. \tag{4}$$

In the case of a high excitation level, when the concentration of the nonequilibrium phonons $n_f \sim n_b$ exceeds the concentration of the equilibrium ones, but $n_f \ll 1$ as before, we obtain

$$n_{ex} = \alpha n_b e^{-\Delta E/2kT}. \tag{5}$$

Thus, the presence of nonequilibrium phonons transforms the quadratic relation between the exciton and biexciton concentrations into a linear one.

2. EXPERIMENTAL PROCEDURE

The experiments were performed on pure n- and p-type germanium with total impurity-center concentration of several units of 10^{12} cm^{-3}. To decrease the rate of surface recombination, the samples were etched after grinding in a polishing etchant and hydrogen peroxide. For the measurements, the samples were freely fastened in a holder and placed in liquid helium.

Two excitation methods were used in the experiments, surface and volume. In the first case the excitation was produced by light pulses of duration 1–1.5 μsec from a type ISSh-100 lamp emitting light in a wide spectral range. The sample thickness did not exceed 1 mm and was so chosen that the time of establishment of the diffusion equilibrium in the sample was smaller than the lifetime of the excitons. All the measurements were performed after such an equilibrium was established. To prevent light from the excitation source from striking the receiver, a combination of water and silicon filters was used.

In the second case, the excitation source was radiation from a dysprosium laser, generating light of wavelength 2.36 μ ($h\nu = 0.53$ eV). The laser was Q-switched with a pulse repetition frequency 400 Hz and pulse duration 40 nsec. The electron-hole pairs were produced in this case as a result of two-photon absorption of the laser emission[19], thus producing volume excitation of samples of thickness up to 1 cm.

The emission spectra were analyzed by an MDR-2 grating monochromator. To register the radiation, we used a low-inertia germanium photodiode and a pulsed synchronous detector, the position of the strobing pulse of which could be varied relative to the excitation pulse in the range from 0.5 to 10^3 μsec. In the study of the radiation relaxation, we used a system of automatic displacement of the detector strobe in the same range of delay times.

The exciton and biexciton lifetimes were determined from the kinetics of the corresponding emission lines. In the investigated samples they ranged from 10 to 60 μsec at helium temperatures. This time is much longer than the excitation-pulse duration, making it possible to determine the concentration of the electron-hole pairs produced in the sample with the aid of photoconductivity measurements performed at room temperature. The concentration was also estimated by starting from the known rate of generation of the excitation sources and, in addition, from an experimental study of the temperature dissociation of the excitons. The data obtained by different methods agreed within a factor 2–3.

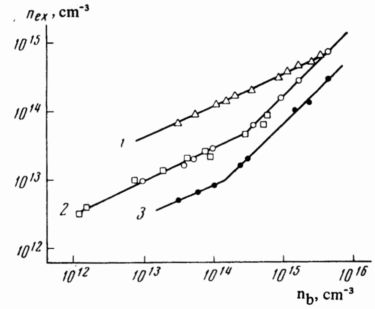

FIG. 1. Plots of the exciton concentration n_{ex} against the biexciton concentration n_b, obtained (1) by varying the time of registration of radiation relative to the instant of termination of the exciting pulse, T = 4.2°K; (2) by varying the level of the surface (○) and volume (□) excitation, T = 4.2°K; (3) by varying the excitation level, T = 3.5°K.

The long lifetimes of the quasiparticles have made it possible to perform all the measurements after a quasiequilibrium relation has been established between the concentrations of the excitons and biexcitons. We note that, both in the investigation of the temperature dependences and in the investigation of the radiation-relaxation kinetics, no deviations from quasiequilibrium relations of the excitons and biexcitons were observed[2]. This allows us to assume that the cross section for the binding of the excitons into a molecule exceeds 10^{-3} cm^2.

3. EXPERIMENTAL RESULTS

We obtained the intensity of the exciton line with quantum energy $h\nu = 0.713$ eV as a function of the intensity of the biexciton line $h\nu = 0.708$ eV at $T = 4.2$°K in a wide range of excitation levels. The data obtained both with volume and with surface excitation are shown in Fig. 1. As seen from the figure, the dependence of the intensity of the biexciton radiation on the intensity of the exciton radiation remains quadratic up to concentrations $n_b \approx 3 \times 10^{14}$ cm^{-3}. At higher excitation levels, a linear dependence is observed, which, as shown in Sec. 1, is due to the influence of the nonequilibrium phonons generated when the excitons become bound into biexcitons.

To verify this hypothesis, we performed experiments in which the excitation level remained constant and the exciton and biexciton concentrations in the sample were varied by delaying the instant of registration of the radiation relative to the instant of excitation. If the phonon lifetime exceeds noticeably the exciton

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[2] If the lifetimes of the excitons relative to interband recombination are not long enough to permit their binding into biexcitons, then the dependence of the biexciton line intensity on the exciton concentration remains quadratic, but the temperature dependence of the intensity ratio of these lines disappears almost completely (the remaining weak dependence is determined by the temperature dependence of the cross section for the production of the exciton molecule). In addition, a distinct kinetics of biexciton emission comes into play.

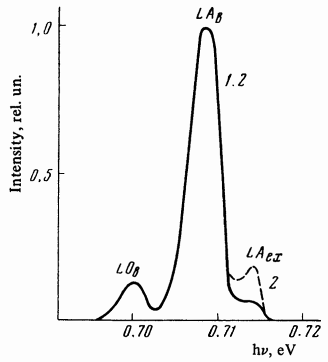

FIG. 2. Germanium emission spectra obtained by the action of one excitation source (1) and by the action of two synchronized excitation sources delayed 80 μsec relative to each other. In both cases, the radiation excited by the second source was registered. The exciton lifetime was 20 μsec and T = 4.2°K. LA_b and LA_{ex} are the radiative recombination lines of the biexcitons and excitons was interaction with longitudinal acoustic phonons, LO_b is the recombination radiation of the biexcitons with interaction with longitudinal optical phonons.

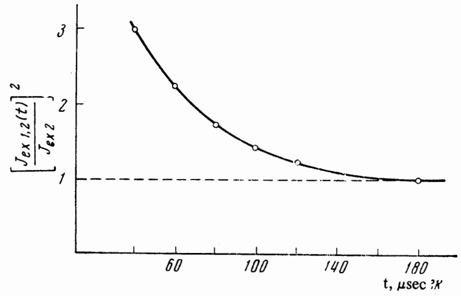

FIG. 3. Nonequilibrium phonon relaxation curve. Sample thickness 0.05 cm, τ_{ex} = 15 μsec, T = 4.2°K.

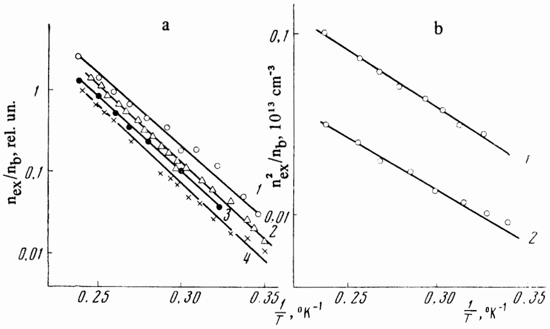

FIG. 4. Temperature dependences of the concentration ratios of the excitons and biexcitons at different excitation levels J; N is the concentration of the electron-hole pairs defined as N = JΔt (sec Sec. 1). a—region of the quadratic relation (4) between the exciton and biexciton concentrations: 1) N = 1.5 X 10^{14} cm^{-3}; 2) N = 10^{14} cm^{-3}; c) N = 5 X 10^{13} cm^{-3}; 4) N = 3 X 10^{13} cm^{-3}. Plots 1 and 3 were obtained with surface excitation, and 2 and 4 with volume excitation. b—Region of linear relation (5) between the exciton and biexciton concentrations: 1) N = 5 X 10^{15} cm^{-3}; 2) N = 10^{15} cm^{-3}, surface excitation. The dependences of γ and α on T have been taken into account.

and biexciton lifetimes, then an increase of the delay leads to a decrease of the exciton and biexciton concentrations while the concentration of the non-equilibrium phonons remains practically unchanged. The results of such an experiment are shown in Fig. 1 (curve 1). In this case the relation remains quadratic in the entire investigated concentration interval, as follows from the effective-mass equation (3) when n_f = const.

The role of the nonequilibrium phonons was confirmed also by experiments in which two light sources, with a relative time delay longer than the lifetimes of the excitons and biexcitons, but shorter than the proposed phonon lifetime, were used to excite the samples. We registered the spectra of the radiation produced when the sample was excited by the second source. All the carriers produced by the first pulse die out by the time the second pulse acts, since the concentration of the phonons generated as a result of the action of the first pulse should remain practically unchanged. Then, as follows from (3), the intensity ratio of the exciton and biexciton lines should increase by a factor $[(n_{f_1} + n_{f_2})/n_{f_2}]^{1/2}$. Figure 2 shows the influence of the first excitation source on the emission spectrum produced by the action of the second source under conditions when the intensity of the second source was one-tenth that of the first.

Obviously, such experiments can be used to measure the lifetimes of long-wave phonons participating in the biexciton production. Indeed, the concentration of the phonons remaining in the sample after a time t following the action of the first excitation pulse can be determined from an analysis of the emission spectrum produced by the second source. If $J_b \gg J_{ex}$, then the intensity of the exciton line varies in such a way that

$$\left[\frac{J_{ex\,1,2}(t)}{J_{ex\,2}}\right]^2 = \frac{n_{f_1}(t)}{n_{f_2}} + 1 \qquad (6)$$

(The subscripts pertain to the excitation sources).

Figure 3 shows the phonon relaxation curve for one of the samples. The decrease of the phonon concentration is well described by an exponential with τ_f = 40 μsec, and the exciton lifetime in this sample is 15 μsec. It was observed in these experiments that τ_f depends significantly on the sample thickness, increasing from several microseconds for samples 0.01 cm thick to 140 μsec for samples 0.2 cm thick. This indicates that the main cause of the annihilation of the phonons is apparently their scattering by the sample surface.

It follows from (4) and (5) that there exist two different activation energies in the exciton-biexciton system. At low excitation levels, when $n_f = n_{f_0}$, this energy is equal to the biexciton dissociation energy E_b. In the opposite case of high excitations, when the ratio of the exciton and biexciton concentrations is determined by the presence of nonequilibrium phonons in the sample, this energy is equal to the "recoil" energy which the biexciton obtains at the instant of its formation. To determine E_b and ΔE, we plotted the temperature dependences of the radiation at different excitation levels. The results obtained with surface and volume excitation are shown in Fig. 4. In the regions of both small and large concentrations, the slope of the curves does not depend on the excitation level and varies only at concentrations at which a transition from a quadratic to a linear dependence is observed in the intensity ratio of the exciton and biexciton lines. The energies E_b and ΔE determined from these experiments turned out to be respectively equal to 3.6–3.8 MeV and 2.0–2.2 meV. The biexciton dissociation energy can also be obtained directly from (4), by substituting in this formula the experimental values of n_{ex} and n_b for a certain (low) excitation level. A numerical estimate yields 3.6 meV, which agrees well with the results of the temperature measurements.

The energy of the phonon generated when the biexciton is produced turns out to equal 1.6 meV in accordance with (1). There is one more method of determining this quantity experimentally. When the excitation intensity is varied, the transition from a linear to a quadratic dependence occurs when the concentration of the nonequilibrium phonons $(n_f - n_{f_0}) \sim n_b$ is approximately equal to the concentration of the equilibrium phonons $n_{f_0} \approx \exp(-\hbar\omega_f/kT)$. Consequently, the biexciton concentration corresponding to the inflection points on curves 2 and 3 of Fig. 1 will depend on the temperature like $\exp(-\hbar\omega_f/kT)$. The value of $\hbar\omega_f$ obtained in this manner turned out to be approximately 1.4 meV, which is close to the value determined above.

It was shown in[7] that in the case of excitation by strongly-absorbed light the state of the sample surface exerts a significant influence on the behavior of the emission spectra at low excitation levels. Experiments on thick samples with volume excitation by dysprosium-laser light are practically free of this shortcoming. Indeed, in this case and in pure samples we did not observe the anomalously abrupt temperature and concentration dependences that were interpreted by the authors of[9,10] as one of the significant arguments that the 0.708 eV line belongs to the exciton rather than the biexciton condensate.

The use of nanosecond light pulses from a dysprosium laser as a volume-excitation source has made it possible to investigate in best fashion the recombination-radiation kinetics. Particular interest attached to measurement of the growth time of the biexciton radiation, which would make it possible to determine the cross section for biexciton production.

Such an investigation of the radiation kinetics at a low excitation level, when the exciton line is predominant, has shown that the biexciton radiation is produced within a time much shorter than the exciton-recombination time. This confirms the conclusion arrived at above that the cross section for binding into biexcitons exceeds 10^{-13} cm^2. Measurement of the radiation attenuation time has shown that at low excitation levels the relaxation time of the biexciton line is approximately double the relaxation time of the exciton line. This result agrees with the conclusions of Sec. 1, formula (4).

4. CONCLUSION

The experimental results obtained in the present investigation demonstrate the biexciton nature of the 0.708-eV line in germanium. Worthy of particular attention is the question of the shape of this line and its energy position. It was indicated in[1] that the position of the maximum and the shape of the analogous emission line in silicon can be explained by assuming that radiative annihilation of one of the excitons in the molecule is accompanied by decay of the other one into a free electron and a free hole. Recognizing, however, that the binding energy of the biexciton in germanium, determined in the present study, is approximately 3.7 meV, and the maximum of the biexciton line is shifted relative to the exciton line by 5 meV, the most probable recombination process seems to be one in which the annihilation of one exciton is accompanied by acceleration of the other as a unit. At the same time, the process with disintegration of one of the excitons, proposed in[1], can make a large contribution to the long-wave region of the spectrum. The fact that the biexciton line has a large long-wave "tail" (Fig. 5) confirms such a radiation mechanism. We note, however, that such a form of the long-wave edge is not critical from the point of view of identification of this line with the exciton molecule or with the exciton condensate, for in both cases we should expect approximately identical regularities if the effective carrier concentration in the exciton molecule is close to the proposed concentration in the condensate[20-23].

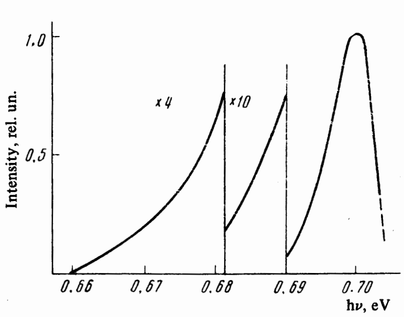

FIG. 5. Long-wave edge of biexciton emission (line LO_b), T = 4.2°K.

The binding energy of the exciton molecule, determined in the present paper, is quite large in comparison with the theoretical values obtained in the effective-mass approximation without allowance for the anisotropy of the effective carrier masses and other features of the band structure of the germanium[24-27]. The data of[11] show that the presence of many valleys is not responsible for such a large binding energy, for in the case when it was possible, by uniaxial compression of the sample in the ⟨111⟩ direction to transfer all the electrons into one valley, the change in the binding energy was negligible.

To explain the possible cause of the anomalously large biexciton binding energy in the germanium, it is of interest to compare it with the value obtained for silicon in[1]. The binding energy of the biexciton in silicon is several times smaller than the exciton Rydberg[3], whereas in germanium is of the order of a Rydberg. Recognizing that the valence bands of silicon and germanium have approximately the same structure, and that the difference in the number of valleys in the conduction band is apparently not significant, it must be assumed that the main factor causing the ratio of the biexciton binding energy to the exciton binding energy to be larger in germanium than in silicon is the difference in the coefficient of anisotropy of the effective masses of the conduction bands of these substances. This conclusion, of course, cannot be regarded as final, and the question of the binding energy obviously calls for further research.

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[3] According to the data of[1], the binding energy is 2 meV. Our preliminary results show, however, that this quantity in silicon is much closer to 5 meV.

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