Deep, free, and bound excitons and biexcitons in GaSe and their collective interaction

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The binding of deep excitons in a molecule and the interaction of these formations with each other and with carriers as well as with deep, exciton-impurity complexes (EIC) were observed for the first time. The parameters of the states and of the processes were determined.

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The appearance of deep excitons (exciton states associated with band extremums that are deeper than the bands forming the fundamental absorption edge) was observed in the absorption spectra of GaSe in Refs. 1, 2. Photoluminescence in the same spectral region was observed in Refs. 3, 4. The interpretation of the results of Refs. 3, 4, due to incomplete experimental data, is unsatisfactory.

This paper reports on our investigation of the photoluminescence spectrum of GaSe at 4.2 and 77 K for excitation by the second harmonic of a ruby laser with a maximum radiation intensity of 2×10^{24} photons cm^{-2} sec^{-1} (1 MW/cm^2) in a 40-nsec flash. The luminescence signal from a DFS-12 spectrograph was recorded by a pulsed synchronous detection system.

Figure 1 (a,b) shows typical radiation spectra for different excitation intensities at 4.2 and 77 K. A part of the differential absorption spectrum of the same samples at 4.2 K, which was obtained by modulating the radiation wavelength, is also shown in Fig. 1b. The dependence of the intensity of the emission lines on pumping at 4.2 and 77 K is shown in Fig. 2.

The experimental data were interpreted on the basis of concepts concerning the interaction of deep excitons at a high concentration, similar to those used for edge excitons. Let us examine each line separately:

Line A, 3.385 eV at 4.2 K, has a linear dependence on pumping of the radiation intensity, coincides with the exciton absorption peak,[1] and follows it with a change in the temperature, i.e., it is the resonance radiation of the deep exciton. The attribution of the 3.361-eV recombination radiation line by the authors of Ref. 3 to the resonance luminescence of the exciton is wrong for the following reasons: first, this radiation does not coincide in energy with the absorption line; secondly, since the excitation in Ref. 3 was two-photon (2×2.34 eV), the emission line of the free exciton in this case should not be observed because of strong self-absorption in the bulk of the crystal.

Line M (3.365 eV at 4.2 K and 3.355 eV at 77 K). The intensity of the M line is approximately porportional to the square of the excitation intensity, $i_M \sim i^2$, to a value of $i = i_0$, and then it becomes linear. These data make it possible to associate the M line with the radiation of a deep biexciton, where recombination occurs via the mechanism proposed by Nikitine[5] for the edge biexciton, and the process kinetics are similar to

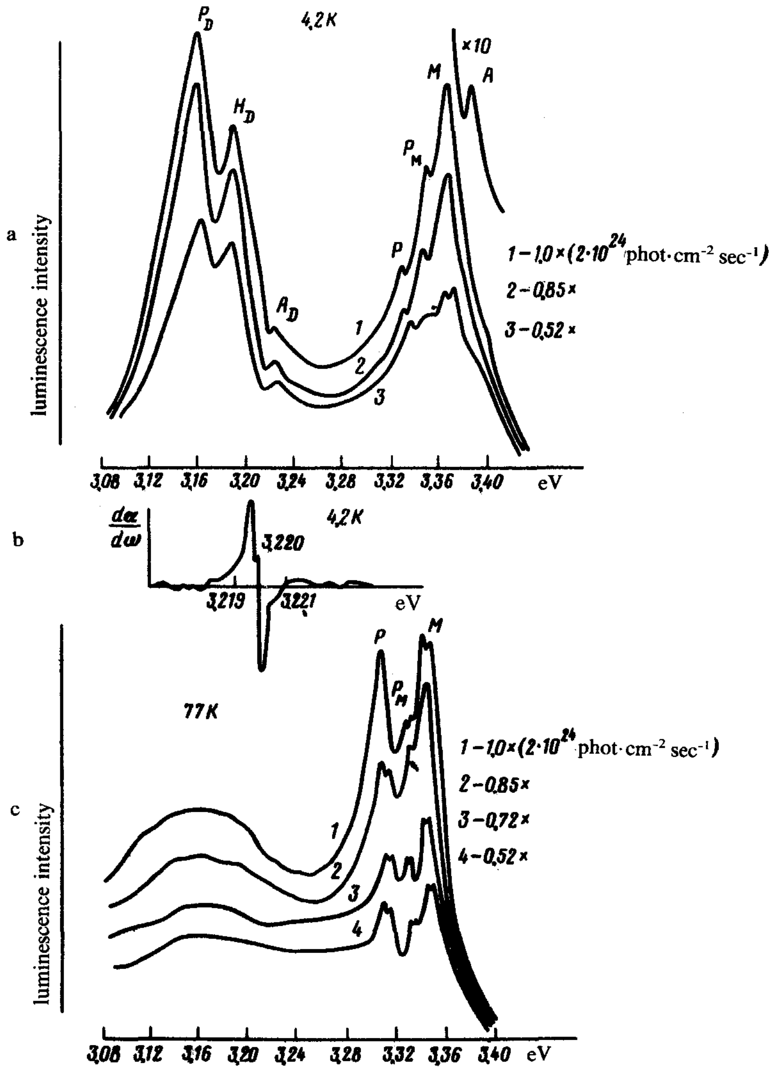
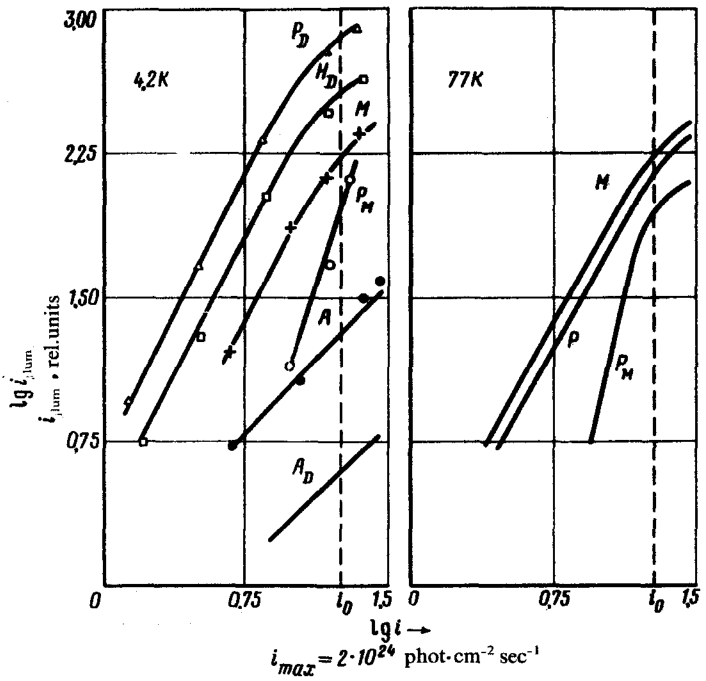


FIG. 1.

those of Knox.[6] Thus, the binding energy of the exciton molecule is $E_B = \hbar\omega_A - \hbar\omega_M = 20$ meV. This interpretation is confirmed by the asymmetry of the M-line contour (steep short-wavelength part and prolonged long-wavelength) and by the fact that its width does not depend on the temperature. The contour is approximated well by the expression[7] with the parameters $\Gamma/kT = 0.9$ and $T = 70$ K. The identification of the M line with phonon repetition[4] is unsatisfactory in light of the new data.

Line P_M (3.345 eV at 4.2 K and 3.335 eV at 77 K). The intensity $i_{P_M} \sim i^4$ to $i = i_0$, and then the exponent decreases; this agrees with the kinetics of radiative recombination via the inelastic collision of two biexcitons with the formation of three excitons and a photon.[7] This is also confirmed by the energy location of the P_M line, which is separated from the M line by $\hbar\omega_M - \hbar\omega_{P_M} = 20$ meV, the biexciton binding energy.



The H line, which is attributable to collisions of deep excitons with carriers, by analogy with this process at the edge[7] whose intensity depends quadratically on the pumping, could also have the same location of the emission maximum. Since only a line with intensity i^4 is observed experimentally, it must be supposed that i_H is much smaller than the intensity of the line due to biexciton collisions.

Line P (3.325 eV at 4.2 K and 3.315 eV at 77 K), $i_P \sim i^2$ to $i = i_0$, then it is linear. The shape of the P-line contour is similar to the contour of the biexciton line. This line can be identified with recombination radiation, which is caused by collisions of deep excitons, by analogy with Ref. 7; this is confirmed by the shift of the P-line maximum toward lower energies as the pumping is increased, due to an increase in the kinetic energy of the carriers that are produced in the course of the exciton interaction. Thus, the exciton binding energy is $E_{\text{ex}} = \hbar\omega_A - \chi\omega_P = 60$ meV. As the temperature increases from 4.2 to 77 K, the intensity of the P line should increase compared with the M line, because of the dissociation of the EIC and associated increase in the density of free excitons; this is actually observed. The indicated temperature dependence also shows that the P line cannot be interpreted as a second phonon repetition of the free exciton radiation.[8] In a number of cases a doublet structure was observed in the M, P_M, and P lines.

Line A_D, H_D, and P_D are observed at 4.2 K, and they broaden and weaken with increasing temperature. Their intensity varies from sample to sample.

Line A_D, 3.220 eV, corresponds to the narrow peak in the absorption spectrum (Fig. 1b), $i_{A_D} \sim i$. All this makes it possible to identify the A_D line with the radiation of a deep exciton, that is bound at a local center.

Line H_D, 3.180 eV, $i_{H_D} \sim i^2$, can be attributed to the radiative recombination of an EIC through inelastic collision with carriers. The energy of the photon emitted in this event[7] is: $\hbar\omega_{H_D} = E_g - E_{ex} - E_D - \frac{1}{2}(m_e + m_h/m_e)\, kT$, and m_e and m_h are the electron and hole masses. Since $\hbar\omega_{A_D} = E_g - E_x - E_D = 3.220$ eV, $(m_e + m_h/m_e)$ $kT = 80$ meV. Using $\mu_{ex} = (m_e m_h/m_e + m_h) = 0.089\ m_0$,[9] we obtain $m_e = 0.089\ m_0$ and $m_h = 20\ m_0$.

Line P_D, 3.160 eV, is attributable to recombination radiation during the collsion of a free, deep exciton and an EIC. Such interpretation corresponds to its spectral location and to the intensity and temperature dependences.

The exciton binding energy was determined from the $E_{ex} = 60$ meV and $\sigma = m_e/m_h = 0.0045$ that were obtained by using the Wehner formula[7]; $E_B^{\text{theor}} = 10$ meV, in good agreement with the value determined above.

Thus, the binding of deep excitons in a molecule and the interaction of these formations with each other and with the carriers, as well as with deep, exciton–impurity complexes were observed for the first time.

[1] V. K. Subashiev, Le-Khac-Binh, and L. S. Chertkova, Solid State Commun. **9**, 369 (1971); V. I. Sokolov and V. K. Subashiev, Phys. Status Solidi B **65**, K47 (1974).

[2] A. Balzarotti, M. Piacentini, E. Burattini, and P. Picozzi, J. Phys. C **4**, 273 (1971).

[3] D. P. Dvornikov, V. M. Salmanov, and I. D. Yaroshetskii, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 17 (1974) [JETP Lett. **20**, 7 (1974)].

[4] V. T. Agekyan, Yu. F. Solomonov, Yu. A. Stepanov, and V. K. Subashiev, Fiz. Tekh. Poluprovodn. **10**, 1776 (1976) [Sov. Phys. Semicond. **10**, 1058 (1976)].

[5] S. Nikitine, A. Mysyrowiez, and J. B. Grun, Helv. Phys. Acta **41**, 1058 (1968).

[6] R. C. Knox, S. Nikitine, and A. Mysyrowiez, Opt. Commun. **1**, 19 (1969).

[7] R. Levy and J. B. Grun, Phys. Status Solidi A **22**, 11 (1974).

[8] E. F. Gross, S. A. Permagorov, and B. S. Razbirin, Usp. Fiz. Nauk **103**, 431 (1971) [Sov. Phys. Usp. **14**, 104 (1971)].