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Fig. 1. Schematic of the luminescence spectrum of a GaP crystal (group A crystals) at $T = 4.2°$K; A —complete luminescence spectrum; B —luminescence caused by interaction of a bound exciton with phonons; C —multiline spectrum of weak narrow lines and the adjacent spectrum of banded edge emission; D —hydrogen-like series of luminescence lines

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Abstract

Full Text

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REGULARLY CONVERGING LINE LUMINESCENCE IN GaP CRYSTALS

The variability of the luminescence spectra of GaP crystals, depending on the conditions under which they are obtained, as experiments ($^{1-5}$) show, indicates the determining influence of impurities and lattice defects on luminescence. In studying luminescence in GaP crystals* we found that in some of them (we shall call them group A) the luminescence spectrum has features not previously observed. The luminescence spectrum of such crystals (Fig. 1A and Fig. 2) contains many lines and can be represented as the superposition of several different spectra (Fig. 1B, C, D).

Fig. 1. Schematic of the luminescence spectrum of a GaP crystal (group A crystals) at $T = 4.2°$K; A —complete luminescence spectrum; B —luminescence caused by interaction of a bound exciton with phonons; C —multiline spectrum of weak narrow lines and the adjacent spectrum of banded edge emission; D —hydrogen-like series of luminescence lines.

In Fig. 1B a spectrum is shown containing lines caused by bound excitons and their interaction with phonons. This spectrum was studied in detail by us in (^{1}). In group A crystals this spectrum has low intensity and the number of observed phonon repetitions is small. Figure 1C shows a spectrum which in group A crystals has considerable intensity, in which a large number of narrow lines are present and on which banded edge luminescence is superposed. This spectrum was studied in a number of works (^{1,4,5}). A detailed investigation of the spectrum of banded edge luminescence was given by us in (^{2}).

Fig. 2. Microphotogram of the luminescence spectrum of GaP crystals (group A crystals) at $T = 4.2$°K

Figure 2: Fig. 2. Microphotogram of the luminescence spectrum of GaP crystals (group A crystals) at $T = 4.2$°K

In addition to the spectra listed, one more spectrum is observed, not described earlier (Fig. 1D), consisting of lines that have a common origin. This is indicated by a number of features. At $T = 4.2$°K in group A crystals the lines of spectrum D are all present together, with greater or lesser intensity, forming a series of doublets, the separation between whose components is the same for all doublets and is 7.6 cm^{-1}. In the first three doublets on the short-wavelength side there is one more, third, weak line. Its distance from the short-wavelength component of the corresponding doublet decreases as one moves into the short-wavelength part of the spectrum. With an increase in temperature from $T = 4.2$°K, when the intensity

Fig. 2. Microphotogram of the luminescence spectrum of GaP crystals (group A crystals) at $T = 4.2$°K

of spectra and begins to decrease, while the intensity of the -spectrum line series, on the contrary, increases. In each doublet the short-wavelength component and the weak line adjacent to it flare up. In addition, as the temperature is raised, owing to the weakening of spectra and and the flaring-up of , a number of still weaker, short-wavelength lines, previously masked by the intense luminescence of spectrum , appear in spectrum .

The process of flaring-up of the lines of spectrum is shown in Fig. 3. At a certain temperature $4.2 < T < 77.3$°K, the lines of spectrum disappear completely, and only the line and band edge luminescence remain in the spectrum (Fig. 3e). A further increase in temperature causes a decrease in the intensity of the lines of spectrum ; the shortest-wavelength lines disappear first, and only line ν_1 and its phonon repetitions remain in the spectrum (Fig. 3d). Line ν_1 in the spectra of a number of crystals can readily be observed even at $T = 77.3$°K, whereas to obtain the remaining lines of the spectrum at this temperature a very large increase in exposure is required. Raising the temperature also causes broadening of the lines of spectrum . All the lines of spectrum are not observed in absorption, which additionally confirms their common origin. From Fig. 1 , Fig. 2, and Table 1 it is seen that these lines form a converging sequence, which can be described by a hydrogen-like series

Table 1

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* All the crystals studied by us were obtained at the Physico-Technical Institute of the Academy of Sciences of the USSR under the direction of N. A. Goryunova, A. S. Borishenskii, G. A. Kalyuzhnaya, and D. N. Tretyakov, to whom we express our sincere gratitude.

Fig. 3

Figure 3: Fig. 3

Wavelengths, frequencies, designations, and interpretation of the lines of the hydrogen-like series in the luminescence spectrum of a GaP crystal

Designation and interpretation	Observed λ, Å	Observed ν, cm^{-1}	Quantum number	Calculated ν, cm^{-1}
$\nu_1'' - \omega_1$	5807	17 221		
$\nu_1 - \omega_2$	5804	17 230		
$\nu_1 - \omega_2$	5798.7	17 245		
ν_1''	5673.7	17 625		
ν_1'	5671.3	17 633	1	17 354
ν_1	5670.0	17 637		
ν_2''	5476	18 260		
ν_2	5474.0	18 268	2	18 295
ν_2'	5473.0	18 271		
ν_3'	5416.3	18 463		
ν_3	5414.3	18 469	3	18 469
ν_3'	5413.8	18 471		
ν_4''	5398.0	18 525		
ν_4	5396.4	18 531	4	18 531
ν_5	5388.4	18 559	5	18 559
ν_6^*	5382.7	18 577	6	18 574
ν_7^*	5381.4	18 583	7	18 583
ν_8^*	5379.3	18 590	8	18 590
ν_9^*	5377.4	18 596	9	18 594

* These lines are observed only at temperatures higher than 4.2°K, when the other lines (spectra and) weaken.

of the form $\nu_n = \nu_\infty - R'/n^2$, with the constants $R' = 1255$ cm^{-1} and $\nu_\infty = 18609$ cm^{-1} (the values of R' and ν_∞ were calculated from the formula using the values ν_3 and ν_4, assuming that they correspond to $n = 3$ and $n = 4$).

As is seen from Table 1, which gives a comparison of the observed frequencies and those calculated from the formula, the agreement for the higher members of the series is satisfactory, but for $n = 1$ and 2 there are considerable deviations, indicating only an approximate hydrogen-like character of this series.*

Fig. 3. Change in the luminescence spectrum of a GaP crystal (crystals of group A) with increasing temperature: *a*—microphotogram of the luminescence spectrum at $T = 4.2$°K; *b*—*d*—microphotograms of the luminescence spectra of the same crystal, obtained with successive increase of the temperature

The existence of this series can be explained if it is assumed that an exciton is bound to the acceptor forming the system of hydrogen-like levels and that, upon decay, it excites an electron to the acceptor levels and radiates the remaining energy, as a result of which a hydrogen-like series of lines appears.** Since at $T = 4.2°$K the acceptor levels are not occupied by electrons, absorption resonant with the lines of the spectrum Γ should not be observed. As shown in Ref. ([8]), acceptor levels in silicon form a hydrogen-like system. Since the band scheme of a GaP crystal is close to the band scheme of silicon, it may be expected that in GaP as well the acceptor levels will form a system of hydrogen-like levels. The ionization energy of the acceptor, determined from the spectrum, is 0.155 eV.

The nature of this acceptor remains unknown. It may be assumed that it is either a silicon atom substituting for phosphorus, or a gallium vacancy. In Ref. ([9]) it was indicated that the energy of an acceptor created by a Ga vacancy is 0.19 eV, which is close to the value 0.155 eV.

In the luminescence spectra of CdS ([10]) and AgJ ([11]) crystals, analogous hydrogen-like series, not observed in absorption, were described.

* At this stage of the investigation we did not introduce corrections into the formula of hydrogen-like dependence to improve the agreement with experiment.

** If this is so, then from the formula $R^1 = \frac{R}{\varepsilon^2}\left(\frac{m_h}{m}\right)$ one can determine the effective mass of the hole in the GaP crystal. Taking for ε the value 8.5 from Ref. ([6]), we obtain $m_h/m_0 = 0.8$. According to the estimate in Ref. ([7]), the effective mass of the hole in a GaP crystal should be somewhat greater than $0.5\,m_0$. The value found by us agrees satisfactorily with the data of Ref. ([7]), taking into account the approximate character of the hydrogen-like formula used by us.

These series were attributed to excitons. But it is highly probable that in CdS and AgJ the series have the same origin as in GaP. Indeed, as was noted in (11), the lines of the AgJ luminescence series are more intense in evaporated films than in single crystals, which indicates their connection with lattice defects.

At $T = 7.73°$ K, in the luminescence spectrum of GaP crystals (crystals of group A), the line ν_1 and a whole series of longer-wavelength lines (phonon replicas) are observed, caused by the transition of an electron to the acceptor level $n = 1$ with the creation of one or several phonons (Table 2, Fig. 4). The phonon frequencies determined from this,

$$\omega_1 = 403\ \text{cm}^{-1}, \quad \omega_2 = 388\ \text{cm}^{-1}, \quad \omega_3 = 219\ \text{cm}^{-1}, \quad \omega_4 = 116\ \text{cm}^{-1},$$

coincide with the phonons determined earlier (1) from spectrum B.

Fig. 4. Microphotogram of a portion of the luminescence spectrum of a GaP crystal (crystal of group A), containing the line $n = 1$ and its phonon replicas, at $T = 77.3°$ K.

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The fact that, for different centers producing the B and G spectra in luminescence, the phonon frequencies coincide testifies to the fact that these

Table 2

Wavelengths, frequencies, and interpretation of the spectrum of phonon replicas of the line
$n = 1$ in the luminescence of a GaP crystal at $T = 77.3^\circ$K

Designation and interpretation	Å	cm^{-1}	Designation and interpretation	Å	cm^{-1}
$\nu_1 + \omega_4$	5651	17 694	$\nu_1 - (\omega_2 + \omega_4)$	5851	17 090
ν_1	5683.7	17 594	$\nu_1 - (\omega_2 + \omega_3)$	5886	16 989
$\nu_1 - \omega_4$	5723	17 478	$(\nu_1 - 2\omega_2)$ and $\nu_1 - (\omega_2 + \omega_1)$	5953	16 798
$\nu_2 - \omega_3$	5755	17 375	$\nu_1 - (2\omega_2 + \omega_4)$	5982	16 716
$\nu_1 - \omega_2$	5811.8	17 206	$\nu_1 - (2\omega_2 + \omega_3)$	6018	16 447
$\nu_1 - \omega_1$	5816.8	17 196			

centers weakly deform the lattice and that the interaction occurs with lattice vibrations, not with local vibrations.

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