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Figure 3 diagram: scheme of luminescence and absorption spectra in a GaP crystal

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Abstract

Full Text

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RESONANT AND NONRESONANT EMISSION OF CENTERS IN A GaP CRYSTAL AND THEIR INTERACTION WITH LATTICE PHONONS

In a number of crystals the absorption and luminescence spectra of local centers consist of continuous bands symmetric with respect to one another (Levshin' s "mirror-symmetry" law (^{1})). As follows from the calculations of Pekar (^{2,3}), Pekar and Krivoglaz (^{4}), and Lax (^{5}), the absorption and luminescence bands arise as a result of the interaction of the local center with lattice phonons and must be arranged mirror-symmetrically with respect to the frequency of the phononless transition, whose intensity is equal to zero. In (^{4}) it is indicated that, under certain conditions, the bands of luminescence and absorption may have a fine structure. As Trifonov (^{6}) showed, when the Stokes losses are small, the frequency of the phononless transition appears with high intensity in the absorption and luminescence spectra. It seems to us that such a case is realized in a GaP crystal. Earlier we reported (^{7}) on a structure found at the edge of the absorption spectrum in a GaP crystal, which we compared with electronic transitions from various valence bands into local states. However, our luminescence studies, described below, showed that this supposition is untenable.

Fig. 3. Scheme of the luminescence and absorption spectra in a GaP crystal: **A** –complete luminescence spectrum; **B** –absorption spectrum; **V** –spectrum of broad luminescence lines associated with acoustic and optical phonons; **G** –spectrum of line luminescence associated with limiting optical phonons; **D**, **E** –spectra of individual luminescence lines and their interaction with limiting optical phonons; **Zh** –multiline spectrum of weak narrow lines and the adjoining portion of the continuous spectrum

As is known (^{8}), only broad bands have been observed in the luminescence spectrum of GaP crystals. We investigated the luminescence of especially pure GaP crystals and found, at $T = 4.2^\circ$ K, about one hundred lines in the luminescence spectrum (Figs. 1 and 2). In the luminescence spectrum one can distinguish a group consisting of several intense lines, which za

is repeated regularly, gradually decreasing in intensity. At long exposures up to seven repetitions were observed. The large number of lines and their different appearance suggest that we are dealing not with a single spectrum in origin, but with the superposition of several spectra. In Fig. 3 the luminescence spectrum is shown schematically (Fig. 3, *A*) and its interpretation as a superposition of individual spectra (Fig. 3, *B*—*Zh*).

Table 1

Wavelengths, frequencies, and interpretation of narrow intense lines in the luminescence spectrum of a GaP crystal

Spectrum	λ, Å	ν, cm^{-1}	Designations and interpretation	Spectrum	λ, Å	ν, cm^{-1}	Designations and interpretation
G	5348.9	18695	ν_0'	D	5855	17079	$\nu_0 - 4\omega_1^0$
G	. . .	. . .	$\nu_0 = \frac{1}{2}(\nu_0' = \nu_0'')$	D	5343.0	18716	ν_1
G	5351.0	18688	ν_0''	D	5345.5	18707	ν_2
G	5462.6	18306	$\nu_0 - \omega_2^0$	D	5455.8	18329	$\nu_1 - \omega_2^0$
G	5466.9	18292	$\nu_0 - \omega_1^0$	D	5458.2	18321	$\nu_2 - \omega_2^0$
G	5581.3	17917	$\nu_0 - 2\omega_2^0$	D	5573.5	17942	$\nu_1 - 2\omega_2^0$
G	5585.6	17903	$\nu_0 - (\omega_1^0 + \omega_2^0)$	D	5576.2	17933	$\nu_2 - 2\omega_2^0$
G	5589.6	17890	$\nu_0 - 2\omega_1^0$	D	5695.8	17556	$\nu_1 - 3\omega_2^0$
G	5705.1	17522	$\nu_0 - 3\omega_2^0$	E	5645.7	17712	ν_4
G	5709.2	17515	$\nu_0 - (\omega_1^0 + 2\omega_2^0)$	E	5772.2	17324	$\nu_4 - \omega_2^0$

Spectrum	λ, Å	ν, cm^{-1}	Designations and interpretation	Spectrum	λ, Å	ν, cm^{-1}	Designations and interpretation
G	5713.9	17501	$\nu_0 - (2\omega_1^0 + \omega_2^0)$	E	5776.8	17311	$\nu_4 - \omega_1^0$
G	5718.0	17488	$\nu_0 - 3\omega_1^0$	E	5904.8	16935	$\nu_4 - 2\omega_2^0$
G	5836	17135	$\nu_0 - 4\omega_2^0$	E	5909.6	16921	$\nu_4 - (\omega_1^0 + \omega_2^0)$
G	5839	17127	$\nu_0 - (\omega_1^0 + 3\omega_2^0)$	E	5914.6	16907	$\nu_4 - 2\omega_1^0$
G	5845	17108	$\nu_0 - (2\omega_1^0 + 2\omega_2^0)$				
G	5850	17093	$\nu_0 - (3\omega_1^0 + \omega_2^0)$				

I. Spectrum G. The spectrum of narrow lines shown in Fig. 3, *G* (see also Table 1, G), begins with two intense lines ν_0' and ν_0'', located at the edges of the absorption line ν_0. The mean value of the frequencies of these lines, $\nu_{\text{av}} = 18692$ cm^{-1}, coincides with the frequency of the absorption line ν_0. We believe that this is one line—the resonance absorption line ν_0, but split into a doublet as a result of reabsorption. The remaining lines of this spectrum can be interpreted as radiative transitions with simultaneous creation of phonons. The narrowness of these lines indicates that the interaction occurs only with limiting frequencies of the vibrational branches. The limiting phonon frequencies determined from this, equal to $\omega_1^0 = 402$ cm^{-1}, $\omega_2^0 = 388$ cm^{-1}, we assign to the optical branches of the crystal. This interpretation agrees with the data of work (^{9}).

II. Spectrum B. This spectrum consists of broad lines (Fig. 3, *B*, Table 2), which do not have resonance lines in the absorption spectrum. The centers of the first $(\nu_0 - \omega_5)$, second $(\nu_0 - \omega_4)$, third $(\nu_0 - \omega_3)$, and fourth $(\nu_0 - \omega_2)$ lines in the first group are shifted relative to the absorption line ν_0 by 14, 112, 225, and 392 cm^{-1}. Further on in the spectrum, this entire group is repeated with frequency ω_2^0, and the repetitions of the line $\nu_0 - \omega_5$ are superposed on the line $\nu_0 - \omega_2$ and its repetitions. The broad lines $\nu_0 - \omega_4$, $\nu_0 - \omega_3$, $\nu_0 - \omega_2$ may be interpreted as a radiative transition with simultaneous creation of phonons corresponding to a large segment of the vibrational branch or, possibly, the entire branch. Observation of broad lines mirror-symmetric to them in the po-

Figure 1

Figure 2: Figure 1

Figure 2

Figure 3: Figure 2

Fig. 1. General appearance of the luminescence spectrum of a GaP crystal at $T = 4.2^\circ$ K, with five repetitions of the group of lines

Fig. 2. Spectrogram and microphotogram, enlarged, of the first three repetitions of the group of lines in the luminescence spectrum of a GaP crystal

absorption confirms the phonon interpretation of these lines. We attribute the broad luminescence lines associated with phonons $\omega_4 = 112$ cm^{-1} and $\omega_3 = 225$ cm^{-1*} to interaction with the acoustic branches of the GaP crystal, which is confirmed in work (^{9}). The broad line associated with the phonon $\omega_2 = 392$ cm^{-1} is correlated by us with the optical branch, whose limiting frequency is $\omega_2^0 = 388$ cm^{-1}.

III. **Spectrum D.** In the spectrum, two weak luminescence lines ν_1 and ν_2 are observed, repeated with greater intensity in combination with the phonon ω_2^0 (Fig. 3, D, Table 1, D).

IV. **Spectrum E.** In this spectrum a sharp emission line ν_4 and its repetitions with limiting phonons ω_1^0 and ω_2^0 are observed (Fig. 3, E, Table 1, E). This line was not observed in absorption.

V. **Spectrum Zh.** The spectrum consists of a large number (up to fifty) of weak narrow luminescence lines and a continuous spectrum adjoining them on the long-wavelength side (Fig. 3, Zh). These lines are observed with greater intensity in crystals obtained from less pure starting materials. In this case the remaining lines of the luminescence spectrum (spectra B, G, D) are not observed. The different nature of spectra B, G, D and spectrum Zh is confirmed by experiments on temperature dependence.

Fig. 4. Microphotogram and general appearance of the absorption spectrum of a GaP crystal at $T = 4.2^\circ$ K

VI. **Spectrum B.** We also investigated the absorption spectrum of a GaP crystal at $T = 4.2^\circ$K (Fig. 4, Table 3). It is noteworthy that the lines ν_0, $\nu_0 + \omega_4$, $\nu_0 + \omega_3$, $\nu_0 + \omega_2$ shift from $T = 77.3^\circ$ K to $T = 4.2^\circ$ K in

Fig. 4. Microphotogram and general appearance of the absorption spectrum of a GaP crystal at $T = 4.2^\circ$ K

Figure 4: Fig. 4. Microphotogram and general appearance of the absorption spectrum of a GaP crystal at $T = 4.2^\circ$ K

such a way that the frequency differences between them remain constant. The identical shift of these lines indicates the commonality of their origin. If the sharp intense absorption line ν_0 corresponds to a purely electronic transition, then, taking into account the structure of the luminescence spectrum, the broad lines $\nu_0 + \omega_4$, $\nu_0 + \omega_3$, $\nu_0 + \omega_2$ must be correlated with an electronic transition with one-simultaneous generation of phonons of broad regions of the vibrational-branch frequencies. The difference in the values of the phonons ω_2, ω_3, ω_4 and ω_2', ω_3', ω_4' is apparently due to the fact that the former refer to vibrations of the lattice in the ground electronic state, and the latter to vibrations of the lattice in the excited electronic state.

Table 2

Wavelengths, frequencies, width* and interpretation of the broad lines of spectrum B in the luminescence of a GaP crystal

λ, Å	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	Designations and interpretation
5353	18679	33	$\nu_0 - \omega_5$
5382	18580	62	$\nu_0 - \omega_4$
5415	18467	18	$\nu_0 - \omega_3$
5469	18287	57	$\nu_0 - \omega_2$ and $\nu_0 - (\omega_5 + \omega_2^0)$
5497	18192	65	$\nu_0 - (\omega_4 + \omega_2^0)$
5531	18080	18	$\nu_0 - (\omega_3 + \omega_2^0)$
5583	17898	58	$\nu_0 - (\omega_2 + \omega_2^0)$ and $\nu_0 - (\omega_5 - 2\omega_2^0)$
5618	17800	70	$\nu_0 - (\omega_4 + 2\omega_2^0)$
5654	17686	25	$\nu_0 - (\omega_3 + 2\omega_2^0)$
5711	17508	58	$\nu_0 - (\omega_2 + 2\omega_2^0)$ and $\nu_0 - (\omega_5 + 3\omega_2^0)$
5747	17400	66	$\nu_0 - (\omega_4 + 3\omega_2^0)$
5779	17302	27	$\nu_0 - (\omega_3 + 3\omega_2^0)$
5841	17120	56	$\nu_0 - (\omega_2 + 3\omega_2^0)$ and $\nu_0 - (\omega_5 + 4\omega_2^0)$
5872	17030	70	$\nu_0 - (\omega_4 + 4\omega_2^0)$

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* The numerical values of the phonon frequencies ω_2, ω_3, and ω_4 given here correspond to the centers of the broad luminescence lines and characterize, on average, the frequencies of the groups of phonons participating in the formation of the given luminescence line.

λ, Å	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	Designations and interpretation
5910	16920	26	$\nu_0-(\omega_3+4\omega_2^0)$
5980	16722	60	$\nu_0-(\omega_2+4\omega_2^0)$ and $\nu_0-(\omega_5+5\omega_2^0)$

* The values of the line widths were obtained by measurement on the spectrogram of the positions of the edges of the luminescence lines.

Comparing the absorption spectrum and the luminescence spectrum Γ, one may conclude that the absorption line ν_0 corresponds to a direct electronic transition, as is evidenced by the luminescence resonant with it. The broad luminescence and absorption lines are located approximately symmetrically with respect to the line ν_0. The Levshin mirror-symmetry law is not fulfilled quite exactly, which is apparently connected with the different magnitudes of the phonons for the excited and unexcited electronic states of the lattice. Here a new interesting fact is found: at the center between the mirror-symmetric bands, both in absorption and in luminescence, a very intense narrow sharp line of the phononless transition (the line ν_0) is observed.

Table 3

Wavelengths, frequencies, width* and interpretation of the absorption lines of a GaP crystal (spectrum B)

λ, Å	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	Designations and interpretation
5366.8	18633		ν_3
5349.7	18692		ν_0
5325.6	18777		ν_5
5312	18823	40	$\nu_0+\omega_4'$
5284	18924	39	$\nu_0+\omega_3'$
5246	19061	30	$\nu_0+\omega_2'$

* For the broad lines, the width values were obtained by measurement on the spectrogram of the positions of the edges of the absorption lines. For narrow lines, no estimate of the width was made.

This experimental result agrees with the theoretical conclusions of Trifonov’ s work (6) on the luminescence of local centers in a crystal lattice. At present it is impossible to draw a definite conclusion about the nature of such centers in a GaP crystal, but it is possible that these centers are bound excitons.

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Note: Figure translations are in progress. See original paper for figures.