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Abstract

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FREE AND BOUND EXCITONS IN GaP CRYSTALS

As has already been reported ([1]), in the absorption and luminescence spectra of GaP crystals a series of narrow absorption and emission lines is observed. Most of these lines are caused by the interaction of electronic transitions with lattice phonons.

Further investigations carried out by us of the absorption spectra of a number of GaP crystals* yielded new results. In the region of the absorption lines $\lambda\lambda$ 5326, 5298, and 5261 Å, found earlier ([1]), we discovered several absorption steps with sharp edges (Figs. 1 and 2). At $T = 77.3^\circ$ K the edges of the steps are located at $\lambda_1 = 5304$ Å, $\lambda_2 = 5264$ Å, and $\lambda_3 = 5229$ Å. The steps discovered by us are clearly observed in those GaP crystals in which all absorption lines are absent (described earlier in ([1])), except for the lines ν_3 and ν_0 (more correctly ν_0', see below). In the spectrum of such crystals these lines are very weak. In those crystals where the line ν_0' is intense, the steps are poorly visible, since phonon repetitions of the line ν_0' are superposed on them. Similar steps arise in the spectrum for an indirect transition to the conduction band ([2]) and to the exciton level ([3]), as follows from theory and as has been confirmed by careful measurements performed for Ge ([4]) and Cu_2O ([5]).

The steps have sharp edges, whereas the edge of the fundamental absorption has no sharp boundary. Therefore we interpret the steps as indirect transitions from the valence band to levels of the free exciton with the participation of phonons (indirect excitons). The three edges of the steps correspond to two optical and two acoustic phonons participating in the transitions; in this case the two optical phonons ω_1 and ω_2 lie so close to one another that the two steps they produce merge into one. The frequencies of the phonons participating in the transition are unknown, since the interaction of the electronic transition may occur with any part of the vibrational branch. It may be supposed that in crystals such as GaP the dispersion of the optical branches, especially the transverse optical

Figure 1

Figure 1: Figure 1

Figure 4

Figure 2: Figure 4

branch, is insignificant ([6]). Therefore the magnitude of the optical phonon ω_2' participating in the formation of the step may be taken equal to the frequency of the optical phonon ω_2, which appears in luminescence ([1]): $\omega_2' = \omega_2 = 390$ cm^{-1}. Assuming that the third edge in the absorption spectrum is due to transitions from the valence band to the lower level of the free exciton with the participation of an optical phonon (i.e., ω_2), we find the energy of formation of free excitons in a GaP crystal to be equal to 18 730 cm^{-1}, or 2.322 eV. This makes it possible, from the positions of the two other steps, to determine the frequencies of the acoustic phonons: $\omega_3' = 260$ cm^{-1} and $\omega_4' = 120$ cm^{-1}. The disagreement between the frequencies of the acoustic phonons ω_3' and ω_4' and the frequencies of the acoustic phonons $\omega_3 = 228$ cm^{-1} and $\omega_4 = 115$ cm^{-1}, found from the luminescence spectrum ([1]), may occur because of significant dispersion of the acoustic branches. The existence of a step-like exci-

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Fig. 1. Microphotograph and general appearance of the steps in the absorption spectrum of GaP crystals at
$T = 77.3°$K

Fig. 4. Microphotograph and general appearance of the luminescence spectrum of a GaP crystal at $T = 4.2°$K. The lines ν_0' and ν_0'' and their first phonon replicas are shown.

of the fine absorption spectrum serves as confirmation that the long-wavelength absorption edge in GaP crystals arises owing to an indirect transition, as was indicated in works ([7,8]).

In work ([7]) the absorption of light in GaP crystals was investigated also in the blue region of the spectrum, and it was established that the absorption here increases sharply; this was associated with the onset of direct transitions from the valence band to the minimum of a higher-lying conduction band. In work ([9]) it was shown that in a Cu_2O crystal, exciton states are formed deep in the conduction band as a result of direct transitions. We attempted to detect similar exciton states deep in the fundamental absorption of GaP crystals.

Fig. 2. Scheme of the absorption spectrum of a GaP crystal at $T = 77.3°$K.

Fig. 2 and Fig. 3

Figure 3: Fig. 2 and Fig. 3

A–complete absorption spectrum, B–spectrum of indirect exciton absorption (absorption steps), V–line ν_0' of a bound exciton and its phonon repetitions, G –other lines of bound excitons

Fig. 3. Microphotogram of the reflection spectrum of a GaP crystal in the blue region at $T = 77.3°\text{K}$

In a crystal $7\,\mu$ thick we succeeded in observing, in the spectrum, a sharp absorption boundary located at $T = 77.3°\text{K}$ at $\lambda = 4340\,\text{Å}$; however, because of the absence of thinner GaP crystals, we were unable to advance farther into the short-wavelength part of the spectrum.

Therefore we turned to reflection spectra. As followed from work ([10]), in the reflection spectrum of a GaP crystal in the region from 2 to 3 eV no noticeable features or reflection maxima were found. In our investigations we used a more refined method for studying reflection spectra, developed in our laboratory by Chzhan Guan-nin ([11]). Studying reflection from a freshly etched surface of a GaP crystal in polarized light near the Brewster angle 70–75° for the GaP crystal), we succeeded, at $T = 77.3°\text{K}$, in detecting in the blue region a sharp and narrow reflection peak located at $\lambda = 4338\,\text{Å}$ (Fig. 3), with a width of 20 Å ($100\,\text{cm}^{-1}$). The unusual narrowness of this maximum in comparison with other maxima, as a rule observed in reflection spectra deep in continuous absorption, gives us grounds to interpret it as a direct transition to the level of a free exciton. The width of this maximum, $100\,\text{cm}^{-1}$, considerable in comparison with the usually observed reflection maxima due to exciton levels in the forbidden band near the long-wavelength edge of the fundamental absorption, can be explained by autoionization caused by the isoenergetic continuous spectrum, occurring-

···lying below it in the conduction band. The absence of other reflection maxima corresponding to higher exciton states can be explained by the fact that in the present case there is a direct, allowed transition, for which the intensities of the higher members of the series fall off rapidly (ˆ3).

The existence of a direct exciton transition shows that the minimum of the second conduction band lies at the center of the Brillouin zone (since the maximum of the valence band is assumed to lie at the center of the Brillouin zone), which confirms the viewpoint of the authors of (ˆ7). The distance from the valence band to the second conduction band, as follows from our measurements, is, to within the exciton binding energy, equal to 2.85 eV.

Let us now return to the phenomena described by us in (ˆ1). In that investigation we reported that in the luminescence spectrum of GaP crystals at $T = 4.2°\text{K}$ we observed a large number of lines, some of which were interpreted as interaction of the electronic transition with lattice phonons (line $\nu_0 = 18\,692\ \text{cm}^{-1}$).

In the luminescence, in place of the absorption line ν_0, two narrow lines ν_0' and ν_0'' were observed ($\nu_0' = 18\,695$ cm^{-1}, $\nu_0'' = 18\,688$ cm^{-1}), which we interpreted as having arisen as a result of reabsorption from the luminescence line, resonant with the absorption line ν_0. However, further investigations carried out on different crystals showed that the explanation of the two lines ν_0' and ν_0'' as a result of reabsorption was incorrect. Indeed, in our further investigations of the luminescence spectra at $T = 4.2$°K it was found that the line ν_0'' is subject to very strong changes in intensity, in contrast to the line ν_0'. In some crystals it is weak and is observed only at long exposures; in other crystals, on the contrary, it exceeds the line ν_0' in intensity. In a number of crystals the intensity of the line ν_0'' is different in different regions of the crystal, while no parallel change in the intensity of the line ν_0' is observed.

With increasing temperature from $T = 4.2$°K and above, the intensities of the lines ν_0' and ν_0'' decrease, the quenching of the line ν_0'' occurring much more rapidly than that of the line ν_0', and the line ν_0'' disappears from the spectrum at a considerably lower temperature, even if at $T = 4.2$°K its intensity exceeded the intensity of the line ν_0'.

All these facts convincingly show that these are two independent lines*. An even more convincing confirmation of this is provided by the investigation of the absorption spectrum at $T = 4.2$°K with large dispersion. In the absorption spectrum two separate lines were found, resonant with the luminescence lines ν_0' and ν_0''.

The phonon repetitions both in the luminescence spectrum (Fig. 4) and in the absorption spectrum (Fig. 2, Table 1) arise mainly from the line ν_0', and not from the line ν_0'', as was assumed in (⌢1). Taking this circumstance into account should give, for the phonon frequencies, values somewhat different from those given in (⌢1). New measurements of the phonon repetitions from the line ν_0' in the luminescence spectrum give the following values for the phonon frequencies: $\omega_4 = 115$ cm^{-1}, $\omega_3 = 228$ cm^{-1}, $\omega_2 = 389$ cm^{-1}, and $\omega_1 = 404$ cm^{-1}. Phonons in absorption have frequency values close to these. The electronic transition ν_0'' apparently interacts more weakly with the lattice, so that phonon repetitions were not observed here in absorption, while in the luminescence spectrum only lines corresponding to the transition ν_0'' with the simultaneous creation of only one or several ω_1 phonons are observed.

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* Investigation of the luminescence spectrum at $T = 4.2$°K with large dispersion (2 Å/mm) showed that the widths of the lines ν_0' and ν_0'' are different: the line ν_0' has a width of 3 cm^{-1}, and the line ν_0'', 0.9 cm^{-1} (the width estimate was made from a microphotogram). This also indicates the different origin of these lines.

The phonon ω_2 does not appear here.* But if the crystal is deformed, luminescence lines appear that are due to the interaction of the transition ν_0'' with both the phonon ω_1 and the phonon ω_2.

At $T = 77.3°$K, in the absorption spectrum of thick GaP crystals two broad absorption lines are observed, at longer wavelengths than the line ν_0' (Fig. 2, Table 1).

These lines can be interpreted as the electronic transition ν_0' with the borrowing of part of the energy from lattice vibrations. The shift of these absorption lines relative to the line ν_0' is equal to 109 cm^{-1} and 230 cm^{-1}, respectively. These values are close to the magnitudes of the phonons ω_4 and ω_3, if one takes into account that the phonon ω_4 has a complex intensity distribution and here only its most intense part appears.

Table 1

Wavelengths, frequencies, designations, and interpretation of the absorption-spectrum lines of a GaP crystal

Designations and interpretation	$T = 4.2°$K λ, Å	$T = 4.2°$K ν, cm^{-1}	$T = 77.3°$K λ, Å	$T = 77.3°$K ν, cm^{-1}
$\nu_0' - \omega_3$	–	–	5430	18 416
$\nu_0' - \omega_4$	–	–	5395	18 535
ν_7	5380	18 587	–	–
ν_3	5366.4	18 634	5382.2	18 580
ν_0''*	5350.6	18 689	5367.4	18 631
ν_0'	5348.9	18 695	5363.2	18 644
ν_5**	5334.3	18 746	5345.2	18 708
ν_6**	5325.6	18 777	5339.2	18 730
$\nu_0' + \omega_4$	5312	18 823	5326	18 775
$\nu_0' + \omega_3$	5284	18 924	5296	18 875
$\nu_0' + \omega_2$	5241	19 080	5256	19 026
$\nu_0' + \omega_1$	5235	19 102	–	–

* At $T = 77.3°$K the line is very weak and is not observed in all crystals.
** Luminescence lines resonant with these absorption lines were not observed.

The presence of luminescence resonant with the absorption lines indicates that a direct transition is taking place here. At the same time, a number of data ([7,8]) show that the minimum of the conduction band and the maximum of the valence band in GaP crystals lie at different values of K. Therefore these lines cannot be interpreted as direct transitions to the levels of free excitons, and it must be assumed that the lines ν_0' and ν_0'' are caused by bound excitons, as was supposed in Ref. ([1]). Knowing the position of the free-exciton level, one can determine their binding energy. For the bound excitons that give rise to the lines ν_0' and ν_0'', the binding energies at $T = 77.3°$K are equal to 0.11 eV and 0.013 eV, respectively. The narrow line ν_3 observed in absorption and luminescence (Fig. 2, Table 1) can also be assigned to a bound exciton, whose binding energy is 0.019 eV.

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* Nothing can be said about the interaction of the electronic transition ν_0'' with acoustic phonons, since, if such an interaction exists, the corresponding phonon replicas will be masked by the more intense phonon replicas of the line ν_0' lying in the same region.

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