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Abstract

Full Text

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LONG-WAVELENGTH EXCITATION OF BANDED EDGE LUMINESCENCE IN GaP CRYSTALS

In a previous communication ⁽¹⁾ on the properties of banded edge radiation in GaP crystals, we showed that the bands of this radiation consist of a whole series of overlapping narrow bands with different afterglow durations. It was also noted there that the banded edge radiation in GaP crystals is intensely excited by red light. In the present work the results of a further study of this phenomenon are given.

If GaP crystals kept at $T = 4.2^\circ$ K are illuminated with light from the wavelength region 7000–6000 Å, green edge luminescence is excited in them. The intensity of this luminescence depends on its intensity when excited by blue light. In those crystals in which the banded edge luminescence is more intense under excitation by blue light, it is also more intense under excitation by red light. Banded edge luminescence can be excited by red light also in those GaP crystals in which, under excitation by blue light, it is weak and is masked by another, more intense luminescence,* described earlier (Fig. 1).

The distribution of intensity in the luminescence bands under excitation by red and blue light is different. If, under excitation by blue light, the short-wavelength maximum ($\lambda_1 = 5604$ Å) in the banded edge luminescence is more intense than the long-wavelength one ($\lambda_2 = 5648$ Å), then under excitation by red light, on the contrary, the long-wavelength maximum predominates in intensity (Fig. 2) and the spectrum becomes similar to the afterglow spectrum ⁽¹⁾. Just as in the afterglow, the maxima of the banded edge luminescence under excitation by red light are shifted to the long-wavelength side in comparison with “blue” excitation and are located at $\lambda'_1 = 5618$ Å and $\lambda'_2 = 5656$ Å. Apparently, “red” excitation is the more effective the longer the lifetime of the corresponding level, and the shift of the maxima is caused by the fact that levels with a longer lifetime are excited more intensely. In contrast to the afterglow maxima, which have steeper edges on the short-wavelength side because components with a short lifetime are cut off, the short-wavelength edges of the maxima under excitation by red

Fig. 2. Microphotograms of the spectra of banded edge radiation of a GaP crystal:

Figure 2

Figure 1: Figure 2

a—excitation by blue light; *b*—excitation by red light; *v*—afterglow spectrum of the same crystal for an afterglow time $(2-5) \cdot 10^{-1}$ s.

* This other luminescence is caused by the interaction of a bound exciton with phonons and was described in detail by us in ⁽²⁾.

with denser light. This shows that the components with short lifetimes are excited by red light as well as by blue light, but with lower intensity.

Under red excitation, besides the striped edge luminescence, a number of narrow lines adjacent to it on the short-wavelength side are also observed (Table 1). The intensity of these lines is small, and they can be observed only at long exposures. These lines are also excited by blue light, but together with other, more numerous lines located in the same spectral region. Thus, red light excites only some of the lines of this multiline spectrum. Possibly these lines belong to the striped edge emission, as we noted in our previous work, but it is also possible that they are caused by other centers not related to the striped edge luminescence, though also capable of being excited by red light.

Table 1

Wavelengths and frequencies of narrow lines in the luminescence spectrum of a GaP crystal excited by red light

λ , Å	ν , cm ⁻¹	λ , Å	ν , cm ⁻¹
5476	18261	5532	18076
5484	18235	5548	18024
5498	18188	5557	17995
5503	18172	5563	17976
5514	18135	5570	17953
5523	18106	5577	17931

The process of excitation of green edge luminescence in GaP by red light can be explained by a certain two-step transition. Two-step transitions discovered in CdS and ZnS crystals have been reported in the literature ⁽³⁾. In those works, long-wavelength excitation was associated with the presence of a copper impurity, which creates levels in the forbidden band; with the aid of these levels, in the course of a two-step transition, an electron passes from the valence band into the conduction band.

It should be noted that in GaP crystals, under “red” excitation, even at the longest exposures, an entire series of other shorter-wavelength lines in the luminescence spectrum, which are intense under excitation by blue light, is not

Fig. 4. Microphotogram of the absorption spectrum of a GaP crystal at $T = 4.2^\circ \text{ K}$ in the red region

Figure 2: Fig. 4. Microphotogram of the absorption spectrum of a GaP crystal at $T = 4.2^\circ \text{ K}$ in the red region

Fig. 1

Figure 3: Fig. 1

observed (Fig. 1). This fact indicates that, in the case of GaP, “red” excitation does not transfer an electron into the conduction band.

Fig. 4. Microphotogram of the absorption spectrum of a GaP crystal at $T = 4.2^\circ \text{ K}$ in the red region

The GaP crystals we studied could contain a certain amount of copper,* and therefore the possibility is not excluded that striped edge luminescence is excited by a two-step transition involving incorporated copper. However, the apparent absence of correlation between the expected co-

* The crystals were synthesized from starting reagents containing copper in an amount $< 3 \cdot 10^{-5}\%$.

Fig. 1. Spectrograms of the luminescence spectra of two different GaP crystals under excitation by blue (a and) and red (and) light

Fig. 3. Spectrograms of the luminescence spectra of an HgJ_2 crystal under excitation by blue (a) and red () light

content and the intensity of the banded edge luminescence of GaP under excitation by red light makes it possible to assume the existence of some other mechanism of two-step excitation of luminescence without the participation of incorporated copper.

We do not know what this excitation mechanism is, but it may be thought that it is also closely connected with the center responsible for the banded edge luminescence. If this is so, then excitation of edge luminescence by long-wavelength light should also occur in “pure” (i.e., without copper impurity) crystals and should be a common property of banded edge luminescence for all crystals.

Table 2

Wavelengths, frequencies, and interpretation of absorption lines of a GaP crystal in the red region at $T = 4.2^\circ \text{ K}$

Fig. 3

Figure 4: Fig. 3

Designation and interpre- tation	λ , Å	ν , cm ⁻¹	Designation and interpre- tation	λ , Å	ν , cm ⁻¹
ν_k	7135.4	14014	$\nu_k +$ ($\omega_3 +$ $2\omega_2$)	6661	15013
$\nu_k + \omega_4$	7077	14131	$\nu_k + 3\omega_2$	6580.7	15196
$\nu_k + \omega_3$	7031	14222	$\nu_k + 4\omega_2$	6417	15583
$\nu_k + \omega_2$	6940.4	14408	ν_{k1}	6992	14302
$\nu_k +$ ($\omega_4 + \omega_2$)	6887	14518	ν_{k2}	6966	14355
$\nu_k +$ ($\omega_3 + \omega_2$)	6837	14626	$\nu_{k1} + \omega_2$	6806	14693
$\nu_k + 2\omega_2$	6757.0	14799	$\nu_{k2} + \omega_2$	6779	14751
$\nu_k +$ ($\omega_4 +$ $2\omega_2$)	6704	14916	$\nu_{k1} + 2\omega_2$	6622	15101

We tested this assumption also on HgJ₂ crystals, in which intense green edge luminescence is observed ⁽⁴⁾. We succeeded in exciting it with long-wavelength (orange) light from the region 5800–6500 Å. In this case, long-wavelength excitation also produces only banded edge luminescence and does not excite at all the line $\lambda = 5320$ Å, which, under blue excitation, exceeds in total intensity the banded edge radiation (Fig. 3).

At $T = 4.2^\circ\text{K}$, in GaP and HgJ₂ crystals under illumination with infrared light we observed a flash of banded edge luminescence analogous to the known flash of green luminescence in CdS crystals. GaP and HgJ₂ crystals illuminated with blue or red light were kept in the dark for up to 10 min. At the moment of illumination with infrared light from the region $0.7\text{--}3\mu$, a flash of banded edge luminescence was observed, indicating the existence of absorption levels in the infrared region. The observation of such a flash in crystals so different in their structure as CdS (wurtzite), GaP (sphalerite), and HgJ₂ (tetragonal lattice) indicates that the existence of absorption levels responsible for the flash is a common property of those crystals in which banded edge radiation is observed.

It should be noted that both the infrared flash and long-wavelength excitation in GaP and HgJ₂ crystals are observed only at sufficiently low temperatures. At a temperature intermediate between that of liquid helium and liquid nitrogen, both disappear. At the same time, the afterglow of the banded edge luminescence in GaP crystals also disappears. However, the banded edge radiation itself does not disappear, since even at $T = 77.3^\circ\text{K}$ it is observed under excitation by blue light. It may be assumed that, with increasing temperature, the lifetimes decrease, which causes the disappearance of the effects described above.

We attempted to detect in GaP crystals absorption bands responsible for long-wavelength excitation. In crystals

GaP, where the green glow under irradiation with red light has a high intensity, we found at $T = 4.2^\circ\text{K}$ two weak narrow absorption lines lying at $\lambda_k = 7135.4 \text{ \AA}$ and $\lambda = 6940.4 \text{ \AA}$, i.e., in the region of red excitation. However, further experiments showed that these absorption lines are in fact apparently not connected with the “red” excitation of the banded edge luminescence. Thus, it was found that these lines are much more intense in crystals in which the intensity of the banded edge luminescence is very small. It should be noted that in such crystals, besides these two lines, a whole series of absorption lines also appears (Fig. 4, Table 2). The regular repetition of the lines makes it possible to assign them to an electronic transition, to which the line $\lambda_k = 7135.4 \text{ \AA}$ corresponds, and to the interaction of this electronic transition with lattice phonons. The phonon values determined from this, $\omega_2 = 392 \text{ cm}^{-1}$, $\omega_3 = 213 \text{ cm}^{-1}$, $\omega_4 = 115 \text{ cm}^{-1}$, coincide with previously found phonon values for a GaP crystal ⁽²⁾. It should be noted that this electronic transition interacts with only one optical phonon.

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