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Corresponding Member of the Academy of Sciences of the USSR E. F. Gross, D. S. Nedzvetskii

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Abstract

Full Text

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FINE STRUCTURE OF THE DECAY TIMES OF BANDS OF EDGE EMISSION IN GaP CRYSTALS

In a number of crystals (CdS (1-3), ZnS (1, 7), CdSe (4), ZnO (5), CaO (6), etc.), near the absorption edge at low temperature, a characteristic emission is observed (edge emission), in which two parts can be distinguished*: an equidistant group of narrow bands ("banded edge emission") and a shorter-wavelength group of narrow lines ("linear edge emission"). The nature of the banded edge luminescence has not been definitively clarified, but it may be regarded as established that it is associated with lattice defects (the model of Schön and Klasens (9) and the model of Lambe and Klick (10)). Griyo connects the existence of the two observed series of edge-luminescence bands with the simultaneous presence of anion and cation vacancies (11).

In a previous paper (12) we reported on linear edge luminescence in GaP crystals (Fig. 3B, , , of paper (12)). It was also noted there that in a number of GaP crystals the luminescence spectrum has a different character. The spectrum consists of a large number of weak narrow lines located in the region 18650-17750 cm^{-1}, and two narrow bands located at 17750 cm^{-1} and at 17350 cm^{-1} (Fig. 3 of paper (12)). Similar luminescence spectra of GaP crystals, containing weak narrow lines and narrow bands adjoining them, were obtained in the work of Fink and Van Vleck (13), and also in the work of Gershenzon, Thomas, and Dietz (14).

We undertook a more detailed investigation of the luminescence spectra of GaP crystals obtained under various crystallization conditions**. Here we present only the results of the investigation of the narrow bands located at 17750 cm^{-1} and at 17350 cm^{-1}, and partially overlapping with a group containing more than one hundred weak narrow lines located in the region 18650-17300 cm^{-1} (Fig. 1). These bands, excited by the lines 4358 and 4047 Å, at $T = 4.2^{\circ}$ K have high intensity in the luminescence spectra of GaP crystals obtained at high temperature.

As a result of the investigations it turned out that the bands are not simple, as we had seen them earlier, but doublet. The first band is resolved into two closely situated bands with maxima at $\lambda = 5604$ Å and $\lambda = 5648$ Å. This group of two bands is repeated in the spectrum with an interval of 400 cm^{-1}, coinciding

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(within the limits of error) with the energy of a longitudinal optical phonon (Table 1). Both in the first group and in its phonon repetitions, the short-wavelength band is more intense than the long-wavelength one. The intensity of the repeating bands decreases rapidly, and at large exposures only three phonon repetitions are observed. The fact that this luminescence consists of two series of narrow bands repeated in the spectrum makes it possible to conclude that it is banded edge luminescence, which agrees with the conclusions of paper (14).

* In paper (8), for a clearer separation of these two parts of edge emission, it was proposed to call the first part "banded edge emission" (an example may be the "green" luminescence of CdS crystals), and the second part "linear edge emission" ("blue" luminescence of CdS crystals). These names are used in the present article.

** These crystals, as well as the crystals investigated by us earlier (12), were obtained at the Physico-Technical Institute of the Academy of Sciences of the USSR by A. S. Borshchevskii, G. A. Kalozhina, and D. N. Tretyakov under the supervision of N. A. Goronova. We express to them our sincere gratitude for all the crystals supplied to us.

In carrying out these studies we noticed that at $T = 4.2^{\circ}$ K GaP crystals possess a long afterglow, sometimes lasting up to several seconds, with the intensity of the afterglow being the greater, the greater the intensity of the banded edge luminescence. Using intermittent excitation, we studied this afterglow in the time interval from 10^{-4} sec. to 2 sec., selecting the corresponding interval by means of a rotating disk with slots.

Table 1

Position of the first (ν_1) and second (ν_2) maxima and their phonon repetitions in the spectrum of the banded edge luminescence of a GaP crystal under continuous excitation

Designation and interpretation	λ, Å	ν, cm^{-1}
ν_1	5604	17844
ν_2	5648	17705
$\nu_1 - \omega$	5738	17427
$\nu_2 - \omega$	5788	17277
$\nu_1 - 2\omega$	5873	17027
$\nu_2 - 2\omega$	5923	16883
$\nu_1 - 3\omega$	6015	16626

Table 2

Position of the first and second maxima of the banded edge luminescence of a GaP crystal at different afterglow times

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Afterglow time, sec.	Maximum	λ, Å	ν, cm^{-1}
$(4—8)\cdot10^{-4}$	1	5623	17784
$(4—8)\cdot10^{-4}$	2	5657	17677
$(1—6)\cdot10^{-3}$	1	5625	17778
$(1—6)\cdot10^{-3}$	2	5659	17671
$(4—7)\cdot10^{-2}$	1	5631	17758
$(4—7)\cdot10^{-2}$	2	5663	17658
$(2—5)\cdot10^{-1}$	1	5642	17724
$(2—5)\cdot10^{-1}$	2	5674	17624
(1.3—2.3)	2	5684	17593

In the afterglow spectrum at times from 10^{-4} sec. and longer, narrow lines were completely absent, and the entire spectrum consisted only of banded edge luminescence; however, this spectrum too underwent considerable changes. We shall consider in detail the behavior of the first two bands, since the remaining bands, which are their phonon repetitions, behave analogously. As is seen from Fig. 2b, already at an afterglow time of $(4—8)\cdot10^{-4}$ sec.* the spectrum differs strongly from the luminescence spectrum observed under continuous excitation. The first and second maxima became considerably narrower and sharper, and their relative intensity changed strongly. Whereas under continuous excitation the first maximum was more intense than the second, in the afterglow, on the contrary, the second maximum has the greater intensity. With a further increase in the afterglow time, the change in the relative intensity of the maxima becomes still more significant. As is seen from Figs. 2c, d, e, the intensity of the first maximum continues to fall and at a time of 1.3–2.3 sec. becomes so small that the first maximum can no longer be observed, and only the second maximum remains in the spectrum (Fig. 2e). The relative intensities of the maxima in the spectra for different crystal specimens may be different. Thus, in the specimen in Fig. 3 (specimen B), at an afterglow time of $(1—6)\cdot10^{-3}$ sec., the first maximum has a greater intensity relative to the second than in the specimen of Fig. 2 (specimen A). But at an afterglow time of $(2—5)\cdot10^{-1}$ sec., the second maximum already predominates in this specimen as well. Since the afterglow intensity decreases strongly with time, to observe the afterglow at long times it was necessary to increase the exposures in order to obtain comparable blackening on the spectrograms.

At the same time, a second intense phenomenon is observed in the afterglow spectrum of the GaP crystal: the maxima of the banded edge luminescence shift toward longer wavelengths as the afterglow time increases (Fig. 2, Table 2). If the maxima under continuous excitation are located–

* The two numbers characterizing the afterglow observation time denote the following: the first number is the moment at which recording of the spectrum begins, the second is the moment at which it ends (during one revolution of the

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Figure 2

Figure 1: Figure 2

Figure 3

Figure 2: Figure 3

disk). Time is measured from the moment at which excitation ceases.

Fig. 1. Microphotogram and general appearance of the spectrum of the banded edge luminescence and the adjacent weak narrow lines of a GaP crystal under continuous excitation.

Fig. 4. Spectrograms of the luminescence and afterglow spectra of different GaP crystals: *a* and *b*—luminescence of two different crystals under continuous excitation; and —afterglow spectra of these same crystals.

are located at 5604 Å and 5648 Å, then under pulsed excitation, for afterglow times of $(4—8) \cdot 10^{-4}$ sec, they lie at 5623 Å and 5657 Å, i.e., they have shifted by 60 and by 30 cm^{-1}, respectively. With a further increase in the afterglow time, the shift of the bands continues, and at times of $(2—5) \cdot 10^{-1}$ sec the maxima are shifted to the long-wavelength side by as much as 120 cm^{-1} and 80 cm^{-1} compared with their position under continuous excitation. At an afterglow time of (1.3—2.3) sec, the first maximum becomes so weak that only the second maximum is observed in the spectrum, its shift to the red reaching 110 cm^{-1} (Fig. 2e, Table 2). All the shifted maxima observed in the afterglow spectra at different times do not go beyond the widths of the bands observed under continuous excitation. It follows from all these facts that each of the bands of the banded edge luminescence consists of a series of bands shifted relative to one another and having different decay times, the decay times in the first band being shorter than in the second.

Fig. 2. Change in the relative intensity and shift of the first and second maxima of the edge luminescence of a GaP crystal (sample A) in the afterglow. *a*—continuous excitation. Pulsed excitation for various afterglow times: *b*—$(4—8) \cdot 10^{-4}$ sec, *v*—$(1—6) \cdot 10^{-3}$ sec, *g*—$(4—7) \cdot 10^{-2}$ sec, *d*—$(2—5) \cdot 10^{-1}$ sec, *e*—(1.3—2.3) sec.

Fig. 3. Microphotogram of the afterglow spectra of a GaP crystal (sample B) for two afterglow times: *a*—$(1—6) \cdot 10^{-3}$ sec, *b*—$(2—5) \cdot 10^{-1}$ sec.

From the literature data it follows that in other crystals the lifetime of the banded edge luminescence is small (for CdS, 10^{-5} sec. ([15])). Apparently, in GaP, owing to certain features in the structure of the crystals, this radiation has a very long lifetime. But since in other crystals as well,

Since in all cases the banded edge emission consists of bands having a width of several tens of cm^{-1}, it may be thought that in all crystals these bands possess

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a fine structure of decay times, but with shorter times.

In the afterglow we were able to observe banded edge emission also in GaP crystals synthesized at lower temperatures. In these crystals the line emission described in ([12]) is intense. The afterglow spectrum in such crystals has low intensity, and we studied it only for afterglow times $(1—6) \cdot 10^{-3}$ sec. The second maximum is considerably weaker than the first and in some crystals lies immediately adjacent to it. In the afterglow an additional weak third maximum appears (Fig. 4).

The dependence of the spectrum of banded edge luminescence on the conditions of crystal synthesis shows that it is connected with lattice defects. It may be thought that this emission is caused by transitions within a donor–acceptor pair (the Williams and Prener model ([16]))* . The transition of an electron captured by a donor to an acceptor takes place through a potential barrier owing to the tunnel effect, and, depending on the distance within the donor–acceptor pair, the probability of such a transition and, correspondingly, the duration of the afterglow change. If the distances within the pair are much greater than the lattice constant, the transition energies are close to one another, and such transitions can give in the spectrum a continuous band with a fine structure of decay times. For small distances within the donor–acceptor pair the energy levels differ greatly from one another, and separate lines adjoining the indicated continuous band should arise in the spectrum**. Indeed, among the multitude of narrow lines adjoining the banded edge emission on the short-wavelength side, several lines are observed whose origin is possibly connected with the banded edge emission. The possibility of such a connection is indicated by our experiments on excitation of luminescence in GaP crystals by red light. When a GaP crystal is illuminated by light from the region $\lambda\lambda$ 6000—7000 Å, the banded edge emission and several narrow lines adjoining it on the short-wavelength side are intensely excited. A more detailed account of these experiments will be given in another communication.

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CITED LITERATURE

1. F. A. Kröger, *Physica*, **7**, 1 (1940).
2. E. F. Gross, M. A. Yakobson, ZhTF, **26**, 1369 (1956).
3. L. R. Furlong, C. R. Ravilious, *Phys. Rev.*, **98**, 954 (1955).
4. E. F. Gross, V. V. Sobolev, ZhTF, **26**, 1622 (1956).
5. J. Ewles, *Proc. Roy. Soc.*, **A34**, 167 (1938).

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6. J. Ewles, *Proc. Leeds Philos. Lit. Soc.*, **3**, 277 (1938).

7. V. M. Kudryavtseva, DAN, **52**, 499 (1946).

8. E. F. Gross, V. V. Sobolev, DAN, **133**, 56 (1960).

9. M. Schön, *Physica*, **20**, 930 (1954); N. A. Klasens, *J. Phys. Chem. Solids*, **7**, 175 (1958).

10. J. J. Lambe, C. C. Klick, D. L. Dexter, *Phys. Rev.*, **103**, 1715 (1956).

11. E. I. Grigio, M. Bansi-Grigio, *Izv. AN SSSR, ser. fiz.*, **22**, 1356 (1958).

12. E. F. Gross, D. S. Nedzvetskii, DAN, **146**, 1047 (1962).

13. A. T. Vink, C. Z. Van Doorn, *Physics Letters*, **1**, 332 (1962).

14. M. Gershenzon, D. G. Thomas, R. E. Dietz, *Proc. of the Intern. Conf. on Semiconductors*, Exeter, 1962, p. 752.

15. J. J. Lambe, *Phys. Rev.*, **98**, 985 (1955).

16. J. S. Prener, F. E. Williams, *J. Chem. Phys.*, **25**, 361 (1956); *Phys. Rev.*, **101**, 1427 (1956); F. E. Williams, *J. Phys. Chem. Solids*, **12**, 265 (1960).

17. J. J. Hopfield, D. G. Thomas, M. Gershenzon, *Phys. Rev. Letters*, **10**, 162 (1963).

* In the recently published paper by Hopfield, Thomas, and Gershenzon ([17]), Williams donor–acceptor pairs are used to interpret the multiline luminescence in GaP crystals.

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

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