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Photoluminescence and Pair Spectrum in Boron Phosphide

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The photoluminescence spectrum of BP was measured at 1.8, 5.0, and 77°K. The 77°K spectrum consists of four bands, one of which appears to be caused by inclusions of phosphorus atoms. At 1.8°K, in addition to the four bands, a donor-acceptor pair spectrum was observed (type-II spectrum) similar to that observed by Hopfield and co-workers in GaP.

INTRODUCTION

IN contrast to the large number of photoluminescence studies performed on GaP and other III–V compounds none has previously been reported on BP. Archer and co-workers[1] observed electroluminescence in BP at 300°K. They found the spectrum to consist of four bands spaced 0.1 eV apart and thought that this spacing might be due to the emission of longitudinal optic (LO) phonons. The absorption edge is near 2 eV[1,2] and is thought to be due to indirect transitions from the top of the valence band at $k=0$ to a conduction band minimum at the X point.

The purpose of this paper is to report the observed photoluminescence spectrum in BP crystals. We will show that one of the emission bands is probably caused by fluorescence of inclusions of phosphorus atoms and that evidence of these inclusions may be seen in the photoluminescence of the other large-band-gap III–V phosphides. It will further be shown that an abundance of fine structure in the 1.8°K luminescence can be explained by the donor-acceptor pair spectra theory of Hopfield *et al.*[3]

EXPERIMENTAL

The BP crystals were grown from a nickel-phosphorus melt and were not intentionally doped. The data reported here were all obtained from one single crystal, but all other crystals from the same batch showed similar luminescence properties. A spark mass spectrographic analysis of two of these crystals showed the following impurities in atomic parts per million. Ni: 3.5, Cl: 1250, S: 700, Hg: 95. It is well known that inclusions of nickel can form inside BP when grown from a nickel melt and we believe that the nickel impurity content is due to such inclusions rather than to nickel as a dissolved impurity. It is also considered unlikely that an ion as large as mercury could be accommodated in the BP lattice. This leaves the major dissolved impurities as chlorine and sulfur. The electrical resistivity of the crystals at 300°K is roughly 300 Ω-cm. Thermal probe measurements suggest a p-type conduction. The photoluminescence measurements were performed as described in Ref. 4. The 1.8°K measurements were done with the sample immersed directly in the liquid helium.

77°K PHOTOLUMINESCENCE

The emission spectrum at 77°K is plotted in Fig. 1. It consists of four emission bands (labeled A, B, C, D) spaced approximately 40 meV apart. The energies of these peaks are given in Table I. There are two interesting features about this luminescence. One is the similarity between the 4 bands observed in photoluminescence at 77°K and the 4 bands reported by Archer *et al.*[1] in the 300°K electroluminescence (E.L.) of BP diodes. These data are included in Table I for comparison. The four maxima reported by Archer are spaced slightly farther apart and, except for the lowest energy band, are located at higher energies than our photoluminescent emissions. The two sets of emissions might be brought into agreement if one assumes that the electroluminescence reported by Archer is due not to true p-n injection but rather to impact ionization. It has been observed[4,5] that radiative recombination peaks may shift to higher energies by as much as a few tenths of a volt when the recombination occurs in a region of high electric field such as occurs in a breakdown process. The larger spacing of Archer's E.L. peaks compared with that observed for the photoluminescence peaks remains unexplained but might be

TABLE I. Energies of emission band peaks.

Band designation	BP photo-luminescence peaks 77°K (eV)	Δ (eV)	BP electro-luminescence peaks 300°K (Archer) (eV)	Δ (eV)
A	1.782		1.972	
		>0.038		>0.086
B	1.744		1.886	
		>0.049		>0.117
C	1.695		1.769	
		>0.037		>0.121
D	1.658		1.648	

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[1] R. J. Archer, R. Y. Koyama, E. E. Loebner, and R. C. Lucas, Phys. Rev. Letters **12**, 538 (1964).

[2] C. C. Wang, M. Cardona, and A. G. Fischer, RCA Rev. **25**, 159 (1964).

[3] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).

[4] M. Rubenstein and F. M. Ryan, J. Appl. Phys. **36**, 2971 (1965).

[5] A. G. Fischer, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964*, edited by B. à la Guillame (Academic Press Inc., New York, 1965), Vol. 4, p. 259.

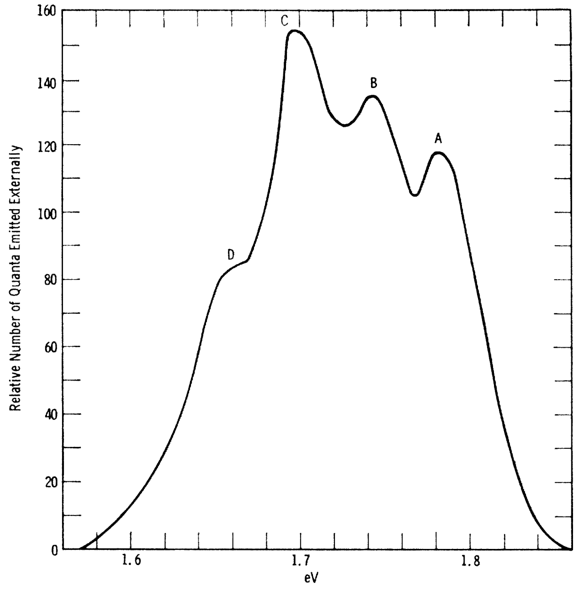

FIG. 1. 77°K photoluminescence of BP.

due in part to changes in the envelope shapes of the emission bands during impact ionization electroluminescence. In the absence of further data we can merely speculate that the four maxima observed by Archer are identical to those observed in photoluminescence. Our crystals were too high in electrical resistivity for observation of electroluminescence.

The second interesting feature of the photoluminescence is that the maximum of band C is located at almost exactly the same energy as the maximum of the luminescence of crystalline red phosphorus at 77°K (Fig. 2).[6] This "coincidence" led us to look for such luminescence in other III–V phosphides. The results are listed in Table II. In all cases the peaks of these emissions occur at nearly the same energy and their envelopes all have similar shapes. Wu's GaP data after renormalization have been plotted also on Fig. 2 to show the similarity. Either these four materials all exhibit one common recombination center whose energy is unaffected by the host, or the data must be explained by what appears to be a very unlikely coincidence. In some cases it is difficult to observe this center since it has a low "apparent quantum efficiency."[7] In the case of GaP, for example, it can only be observed if the more efficient "deep donor" centers are not present in large numbers. Wu[8] reports seeing this emission in only one undoped n type GaP crystal out of many he studied.

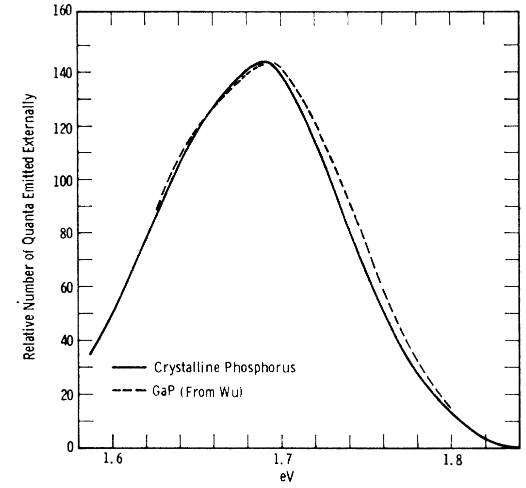

FIG. 2. Comparison of the 77°K photoluminescence of crystalline phosphorus and GaP.

It is our opinion that in all of these cases the 1.69-eV luminescence is due to microscopic aggregates or inclusions or phosphorus within the crystals. The possibility of a surface coating of phosphorus on our BP crystals causing this luminescence can be ruled out since the luminescence was not altered following a nitric acid wash which would be expected to remove any free phosphorus.

TABLE II. Luminescence in phosphides.

Material	77°K photoluminescence peak (eV)
Crystalline P	1.692
BP	1.695
GaP[a]	1.693
AlP	1.69

[a] See Ref. 8.

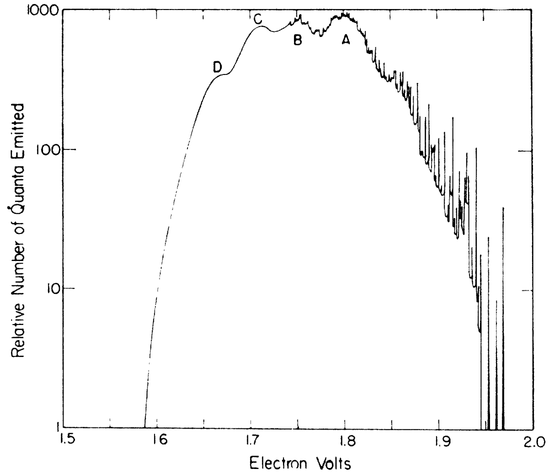

FIG. 3. 1.8°K photoluminescence of BP.

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[6] M. Rubenstein and F. M. Ryan (unpublished).

[7] The term "apparent quantum efficiency" is used here because one can imagine a situation in which a small percentage of the sample volume could be occupied by efficiently luminescing phosphorus aggregates. Their total luminescent efficiency per unit volume would appear low.

[8] Bevan P. F. Wu, Stanford Electronics Laboratories Technical Report No. 5064-3, 1964 (unpublished).

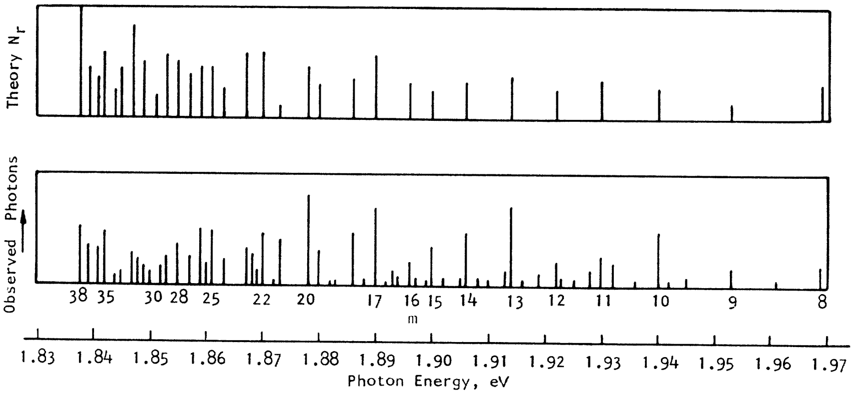

FIG. 4. The match between the values of $N(r)$ and the observed intensities (type-II pair spectrum). m is the "shell" number and is an integer related to the pair separation by $r=(8m-5)^{1/2}a_0/4$ for a type-II pair spectrum.

1.8°K PHOTOLUMINESCENCE

The luminescence at 1.8°K is plotted in Fig. 3. Fine structure appears at this temperature in the two higher energy emission bands (A and B) and over 120 emission peaks (lines) are observed. The total number of lines observed was limited by instrumental resolution. In order to maintain a favorable signal-to-noise ratio during the experiment it was necessary to open the spectrometer slits to an average resolution of 1 Å. Thus emission peaks located closer together than 1 Å are unresolvable and appear as one line or a continuum. This affects the lower energy peaks most as they are spaced closer together and grow out of a larger fluorescence background envelope than the higher energy lines.

Similar complicated low-temperature emission spectra have been observed in GaP by Hopfield *et al.*[3] They showed that the majority of the lines are due to recombination of electrons and holes which are trapped on distant donor-acceptor pairs. The energy of an electron-hole pair (the fluorescence energy) on an isolated distant donor and acceptor separated by a distance r is

$$E(r)=E_{\mathrm{gap}}-E_D-E_A+e^2/\epsilon_0 r-(e^2/\epsilon_0)(\alpha^5/r^6)+\cdots, \quad (1)$$

where E_D and E_A are the isolated donor and acceptor binding energies, ϵ_0 the static dielectric constant, and α the effective van der Waals coefficient for a neutral donor–neutral acceptor interaction. In a crystal lattice only discrete values of r are possible. This gives rise to the discrete series of fluorescence lines as a function of energy characteristic of a given donor-acceptor pair. The intensity of each line is proportional to the number of pairs $N(r)$, at that distance weighted by the fluorescent efficiency as a function of pair separation. The limitations of this theory are discussed in Hopfield's original paper. In the zinc-blende lattice there can be three different types of pair spectra depending upon the types of sites occupied by the donors and the acceptors. Type-I spectra occur if both donor and acceptor are located on the same type of substitutional or interstitial site (i.e., both on boron sites, phosphorus sites, or in the octahedral holes in either the boron or phosphorus sublattice). Type II occurs if the donor and acceptor are on different sublattices (i.e., one substitutional on each sublattice, one substitutional and one in the octahedral hole in the other sublattice, and one in the octahedral hole in each of the two sublattices). Type III occurs if both donors and acceptors are on the same sublattice, one substitutional and the other in the octahedral hole.

Figure 4 shows the agreement between the observed lines and intensities in BP with the theoretical values of $N(r)$ for type-II pair spectra. The amplitudes of the observed lines are obtained by subtracting the broad fluorescence background envelope from the total amplitude of the peaks. The match here was only achieved for the higher energy lines in the spectrum of band A (up to approximately $m=38$). m is the "shell" number and is an integer related to the pair separation by $r=[(8m-5)/16]^{1/2}a_0$ for a type-II spectrum. The line spectrum becomes complicated by what appear to be pair lines from band B overlapping the band-A pair lines at the lower energies and a further analysis was impossible with our experimental resolution. The spectrum was also taken at 5°K, and sharp line spectra were observed but no match was attempted with these data.[9] The experimental line spectrum in Fig. 4 contains extra lines that are not present in the theoretical $N(r)$ plot. Some of these are probably due to sources other than a pair spectrum, such as excitons bound to single impurities; some others are undoubtedly due to

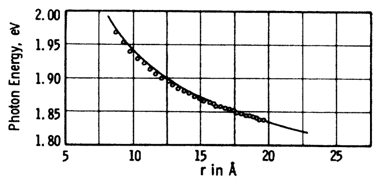

FIG. 5. The energy of the lines plotted against the pair separation in Å. The solid line follows Eq. (1) for $\epsilon_0=6.9$ and $\alpha=0$.

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[9] It is desirable to perform an experiment of this type at the lowest possible temperature to avoid more complex spectra due to thermal excitation of low-lying states as discussed in Ref. 3.

pair recombination from inequivalent sites on the same *m* shell. For a type-II pair spectrum all of the shells from $m=8$ to 38 have two or more inequivalent sites except for $m=9$, 12, 15, 21, and 30.

Figure 5 shows a comparison between the observed line energies and the values predicted by Eq. (1) for a type-II spectrum assuming a lattice constant of 4.538 Å, a dielectric constant of 6.9, and $\alpha=0$. The true value of the static dielectric constant is not known for BP. A direct measurement was not possible because insulating crystals of BP of adequate size were not available. Since BP is almost completely covalent in nature,[2] the static dielectric constant is probably very close in value to the high-frequency dielectric constant which is equal to the square of the optical index of refraction in a region of low absorption. We obtained a value of 2.6 for the index of refraction by measuring the Brewster angle on a 5-mm-thick crystal (really too thin for this type of measurement) using reflection from an as-grown face. Stone and Hill[10] estimate the index to be between 3.0 and 3.5 from image displacement and Wang[11] estimates it at 3.1 from reflectivity measurements. None of these values are very reliable so we chose our value of $n=2.6$ for plotting Eq. (1) on Fig. 5.

CONCLUSION

Boron phosphide is an excellent material for studying radiative recombination of excitons at low temperatures. As better control is achieved over the introduction of impurities into BP it should be possible to identify some of the "extra" spectral lines we observed and, in addition, to introduce new types of pair spectra.

Our evidence for the luminescence of phosphorus inclusions in the III–V phosphides suggests that one should look for such photoluminescence in other phosphorus-containing luminescent compounds such as ZnP_2 or the many luminescent phosphates.

ACKNOWLEDGMENTS

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APPENDIX

Although the previous publications of pair spectra have included a few illustrative values of $N(r)$ for type-I and -II spectra, a complete list of values has not been published. As the calculation of the $N(r)$ values is somewhat time-consuming, we are including here the $N(r)$ values for all three pair-spectrum types in the zinc-blende lattice. Values of *m* from 8 to 67 are listed in Table III. Values of *m* less than 8 gen-

TABLE III. $N(r)$ values of three pair-spectrum types in zinc-blende-lattice.

Shell No. *m*	Type I	Type II	Type III
8	6[a]	36	48
9	36	12[a]	24
10	24	28	48
11	24	36	...[b]
12	24	24[a]	30
13	72	36	32
14	...[b]	36	72
15	48	24[a]	...[b]
16	12	24	48
17	48	60	48
18	30	36	24
19	72	28	...[b]
20	24	48	96
21	48	12[a]	24
22	24	60	72
23	48	60	...[b]
24	8[a]	24	54
25	84	48	48
26	24	48	72
27	96	36	...[b]
28	48	48	48
29	24	60	72
30	...[b]	24[a]	72
31	96	52	...[b]
32	6[a]	84	96
33	96	48	24
34	48	24	96
35	70	60	...[b]
36	36	36	48
37	120	48	56
38	24	96	96
39	48	36	...[b]
40	24	72	102
41	48	48	72
42	48	36	48
43	120	72	...[b]
44	24	60	144
45	120	48	48
46	...[b]	52	48
47	96	96	...[b]
48	24	36	48
49	108	60	72
50	30	96	168
51	48	24[a]	...[b]
52	72	72	96
53	72	108	72
54	32	24[a]	72
55	148	48	...[b]
56	...[b]	60	96
57	96	72	48
58	72	96	120
59	72	84	...[b]
60	48	60	78
61	120	48	48
62	...[b]	108	144
63	144	36	...[b]
64	12	52	144
65	48	72	120
66	48	60	48
67	168	108	...[b]

[a] No inequivalent sites in shell.
[b] No shell corresponds to this *m* value.

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[10] B. D. Stone and D. E. Hill, Phys. Rev. Letters 4, 534 (1960).

[11] C. C. Wang (private communication).

TABLE IV. *AB*, donor-acceptor combinations that give rise to the three pair-spectrum types.

Type I	Type II	Type III
Sub. *A*–Sub. *A* Int. *A*–Int. *A* Sub. *B*–Sub. *B* Int. *B*–Int. *B*	Sub. *A*–Sub. *B* Int. *A*–Int. *B* Sub. *A*–Int. *B* Sub. *B*–Int. *A*	Sub. *A*–Int. *A* Sub. *B*–Int. *B*

erally do not correspond to stable pairs, so no $N(r)$ values are listed for these (exciton-donor or exciton-acceptor interaction becomes larger than the pair complex interaction at close distance). The relationships between shell number m and pair separation r are

$$\text{Type I:} \quad r=(2m)^{1/2}a_0,$$
$$\text{Type II:} \quad r=(8m-5)^{1/2}a_0/4,$$
$$\text{Type III:} \quad r=(2m+1)^{1/2}a_0.$$

In a zinc-blende lattice, for a compound *AB*, the donor-acceptor combinations that give rise to the three types of spectra are listed in Table IV.

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Diffusion of Triplet Excitons in Anthracene Crystals

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Diffusion of triplet excitons in anthracene crystals has been detected by time-dependent studies of the delayed blue fluorescence under varying spatial distribution of the exciting red light. The delayed fluorescence which results from triplet-triplet annihilation was used as a passive probe for detecting the triplets. The observed changes in the time dependence of the delayed fluorescence can be interpreted uniquely as due to triplet-exciton migration, and can be described by a diffusion equation. A diffusion constant of 2×10^{-4} cm^2 sec^{-1} was obtained for triplet diffusion in the *ab* plane of anthracene crystals at room temperature.

INTRODUCTION

THE exciton, an excited state of a crystal which transports electronic excitation energy without transport of charge, has been studied extensively both theoretically and experimentally.[1,2] The concept of the exciton has led to the understanding, at least in principle, of the optical properties of numerous nonmetallic crystals. The experimental status of the energy-transport properties of the exciton, however, is not clear-cut.[1,2] Until recently the study of exciton motion was confined to systems in which the exciton diffusion length was less than the wavelength of light and, consequently, values of diffusion length have been inferred indirectly.[1,2]

Recently, two of the present authors[3] reported a diffusion length of about 10 μ for metastable triplet excitons in anthracene. In these steady-state experiments the exciton was used as its own detector by observing the delayed blue fluorescence resulting from the triplet-triplet annihilation process. It has been established that two triplets which get sufficiently close annihilate each other, creating a blue-fluorescing singlet exciton, and that the resulting delayed fluorescence per unit volume of crystal is proportional to the square of the triplet-exciton concentration.[4–7] As the excitons spread out due to diffusion, the total delayed fluorescence intensity decreases. The actual experiment was carried out by irradiating the anthracene crystal with red light from a continuous helium-neon laser with a Ronchi ruling (a grating with alternating opaque and transparent strips) between the laser and the crystal. With sufficiently fine gratings the intensity of the blue emission did decrease, proving the presence of excitons within shadow regions of the crystal. It was assumed that the spreading of excitons into the shadow regions was due to diffusion. The alternative interpretation, that the presence of excitons within the shadow regions was due to direct generation of excitons by diffracted and scattered photons rather than diffusion, could not be ruled out completely.

In the present work on anthracene crystals, results of time-dependent experiments are presented in which the relatively slow spreading of triplet excitons can be dis-

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* Contribution No. 1186.

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