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*M. V. Lomonosov State University, Moscow (a)*  
*and A. M. Gorki Pedagogical Institute, Kiev<sup>1</sup> (b)*

## Cathodoluminescence of Cadmium Diphosphide Crystals

By

V. VAVILOV (a), I. GORBAN (b), N. KORETS (b), M. TENNAKUN (a),  
I. TYCHINA (b), and M. CHUKICHEV (a)

An investigation is made of the cathodoluminescence spectra of CdP<sub>2</sub> crystals in the temperature range 6 to 300 K. A pulsing beam of high energy electrons (40 kV) is used in the experiment. The samples investigated are undoped, heat annealed in vacuum or saturated vapours of cadmium, and also doped with As and Bi, elements isoelectronic to phosphorus. The experimental results show that the fine structure present in the higher energy wing (2.02 to 2.14 eV) depends on the concentration of the uncontrolled nitrogen impurity in CdP<sub>2</sub>. Atoms of nitrogen give rise to exciton-impurity complexes, leading to intense narrow peaks in the spectrum of cathodoluminescence. Their location and nature are shown in a table.

Приведены результаты исследований спектров катодолуминесценции кристаллов CdP<sub>2</sub> в температурном интервале (6 до 300 К). Возбуждение кристаллов проводилось пульсирующим пучком электронов. Для измерений использовались образцы CdP<sub>2</sub>-исходные, отожженные в вакууме, в насыщенных парах кадмия и легированные изоэлектронными элементами As и Bi. Измерения показали, что при низких температурах тонкая структура спектра (энергетический интервал 2,02 до 2,14 eV) зависит от концентрации неконтролируемых примесей азота в CdP<sub>2</sub>. Атомы азота создают экситонно-примесные комплексы, которые проявляются в спектре в виде узкой интенсивной линии, их положение и природа указаны в таблице.

### 1. Introduction

Radiative recombination spectra of monocrystals CdP<sub>2</sub> were considered in [1 to 7]. From the above works, it appears that the edge luminescence at 4.2 K consists of a well defined fine structure in the energy region of the spectrum between 2.08 and 2.14 eV. According to [1], the above-mentioned fine structure is due to radiative recombination, with the participation of exciton-impurity complexes and donor-acceptor pairs. The investigation of radiative recombination after excitation with an electron beam revealed that the radiative recombination spectrum in the band 2.00 to 2.08 eV is caused by radiative recombination with the participation of free excitons, bound excitons, as well as free electron-hole pairs [2].

Two new bands with maximum at 2.141 and 2.150 eV were observed in the spectrum of radiative recombination after excitation with an electron beam [8]. The appearance of these bands was attributed to the radiative recombination of free excitons and electron-hole pairs [2]. In the photoluminescence spectrum [1], a broad band without structure, with maximum at 1.82 eV, was observed. Its behaviour was studied in the luminescence spectrum obtained after excitation with an electron beam [10]. The above-mentioned band is attributed to the recombination at centres formed of the

<sup>1</sup>) Ul. Pirogova 9, SU-252030 Kiev, USSR.

associates of twice ionized cadmium vacancies and once ionized donors occupying neighbouring positions in the crystal lattice [10]. Luminescence of specially doped crystals was studied in detail in [4]. The observed luminescence spectrum was explained as due to intra-centre transitions as well as to transitions between impurity centres caused by the dopants. Doping with copper [5] and also doping with zinc and bismuth [6] gave rise to a new region of luminescence with maxima at 1.12, 1.24, and 0.62 eV, respectively. This region of luminescence is considered to be caused by donor-acceptor transitions between impurities, where the dopants in the crystal lattice represent the donors and structural defects the acceptors.

In the above-mentioned paper the knowledge on the nature of the luminescence spectra is fragmentary and not explained sufficiently. Therefore the aim of our paper is to study in detail the energy spectrum and its nature in  $\text{CdP}_2$  crystals.

## 2. Method of Experimental Investigation

In our measurements we employed monocrystals obtained by the Bridgman method. Doping was performed by the introduction of dopants in the vapour phase to the main components that were present in the vapour phase in stoichiometric proportions. Heat treatment of the crystals was performed at 700 to 730 K for 50 h in vacuum and vapours of Cd and P. Except for the crystals of  $\text{CdP}_2$  heat-treated in Cd vapours, all undoped crystals obtained by the Bridgman method as well as heat-treated as above in vacuum showed p-type conductivity with resistivity of  $10^4$  to  $10^{10}$   $\Omega$  cm.

An electron-beam apparatus [8] was used in our experimental measurements. All results were obtained for the following values of the parameters, in the exciting electron beam: current density in the electron beam  $10^3$  to  $10^4$  A/m<sup>2</sup>, duration of the pulse  $3 \times 10^{-7}$  ps, mean energy of an electron in the beam 40 keV.

## 3. Experimental Results and Discussion

Fig. 1 and 2 show the cathodoluminescence spectra at 6 K for undoped and thermally treated monocrystalline  $\text{CdP}_2$  samples. Table 1 contains information on the nature of the peaks in the fine structure present in the cathodoluminescence spectrum. Several series of crystals were investigated. We note that character and intensity of the various maxima appearing in the cathodoluminescence spectra for crystals of a single series did not differ appreciably. The intensity of the maxima is appreciably affected by the quality of the matrix components (i.e. cadmium and phosphorus) and also by the heat treatment of the  $\text{CdP}_2$  crystals.

In Fig. 1 the cathodoluminescence spectra at 6 K for two series of crystals are shown. The decreasing intensity of luminescence of the series prepared from low-quality main components (Fig. 1 a) may be attributed to the increase in the concentration of nonradiative recombination centres caused by the presence of uncontrolled impurities in the crystal lattice. The decrease in quantum output for thermally treated crystals (Fig. 1 b) is mainly due to the change in the concentration of structural defects caused by vacancies and interstitial atoms. Structural defects in  $\text{CdP}_2$  in direct proportion to their concentration give rise to channels of intensive nonradiative recombination.

The nature of the peak with maximum at 2.141 eV was studied in detail in [2] where it was considered to be due to the radiative recombination of free excitons. The line at 2.134 eV and its phonon replica were studied in [2, 8], according to their observations the line at 2.134 eV was more intensive than the line at 2.128 eV. But according to our results the position of the maximum of the line is at 2.133 eV (instead of

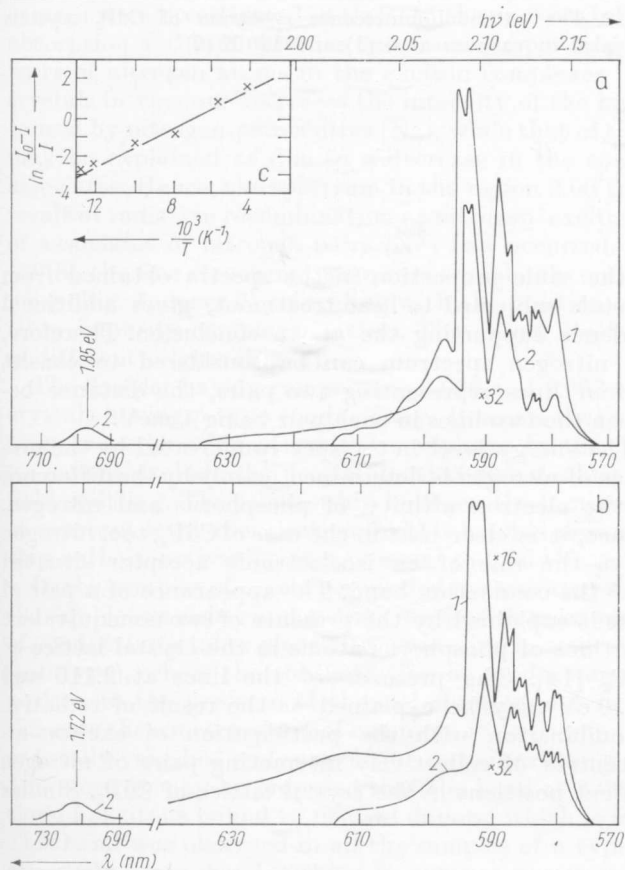


Fig. 1. The cathodoluminescence spectrum of cadmium diphosphide crystals at 6 K. a) (1) crystals grown from high-quality, (2) from poor-quality components; b) (1) crystals annealed in vacuum, (2) in saturated cadmium vapour. c) The temperature dependence of the luminescence intensity for the 2.096 eV line

2.134 eV in [2, 8]), its intensity is weaker than that of the 2.129 eV line (position of our maximum corresponding to the 2.128 eV one in [2, 8]).

The authors of [3] investigated all the bands of the spectrum and concluded that the recombination centres corresponding to the above peaks were exciton-impurity complexes. GaP [11] and tetragonal  $\text{ZnP}_2$  [12] contain the uncontrolled impurity nitrogen which is isoelectronic with phosphorus. In analogy to the above we can assume that in  $\text{CdP}_2$ , too, phosphorus is isoelectronically replaced in the crystal lattice by nitrogen. Hence, the appearance of the lines 2.133 and 2.128 eV is caused by the presence of nitrogen in the crystal lattice of  $\text{CdP}_2$ . The lines at 2.133 and 2.128 eV are not separately identified at temperatures higher than 50 K. This is due to the overlapping of the two lines, resulting from the broadening of the bands as the temperature increases. The two lines at 2.123 and 2.119 eV are at a distance of 10 meV from the non-phonon lines 2.133 and 2.129 eV, respectively. The intensities of the above four lines changed identically for each series of crystals investigated. Therefore it is possible to conclude that the above four lines appear as a result of radiative recombination at the same centre. Furthermore, the fall in intensity of these four lines

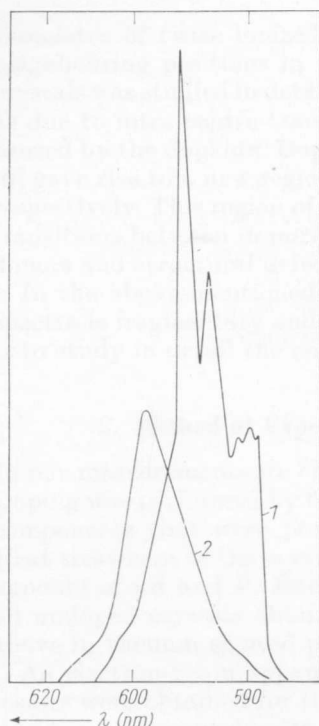


Fig. 2. The cathodoluminescence spectrum of  $\text{CdP}_2$  crystals annealed in vacuum at 6 (1) and 120 K (2)

in the same proportion in the spectra obtained from crystals subjected to heat treatment, gives additional evidence supporting the above conclusion. Therefore, the nitrogen spectrum can be considered to consist of four lines representing two pairs, the distance between the two lines in each pair being 4 meV.

The energy level in the spectrum created by the presence of nitrogen is determined mainly by the difference in the electron affinity of phosphorus and nitrogen. Hence, it is clear that in the case of  $\text{CdP}_2$ , too, nitrogen plays the role of an isoelectronic acceptor situated near the conduction band. The appearance of a pair of lines is explained by the presence of two nonequivalent positions of phosphorus atoms in the crystal lattice of  $\text{CdP}_2$  [14]. The presence of the lines at 2.116 and 2.110 eV may be explained as the result of radiative recombination with the participation of exciton-nitrogen complexes, formed at centres of collectively interacting pairs of nitrogen atoms occupying two nonequivalent positions in the crystal lattice of  $\text{CdP}_2$ . Similar

Table 1

Location of maxima at 6 K in the cathodoluminescence spectrum of undoped  $\text{CdP}_2$  crystals

No.	$\lambda$ (nm)	$h\nu_{\text{max}}$ (eV)	$E_g - \Delta E_{\text{ex}} - h\nu_{\text{max}}$ (eV)	comment
1	578.9	2.140	0	free exciton, $E_{\text{ex}} = 16$ meV
2	580.8	2.133	7	exciton localized at N centre
3	581.9	2.129	11	
4	583.5	2.123	17	exciton localized at N centre + phonon
5	584.6	2.119	21	
6	586.1	2.114	26	exciton localized at N centre
7	587.2	2.110	30	
8	591.0	2.096	44	exciton localized at acceptor
9	592.0	2.093	47	
10	596.0	2.079	phonon replica	
11	604.0	2.051		
12	608.6	2.036		
13	612.0	2.024		
14	615.0	2.015		after heat treatment in vacuum
15	720.0	1.721		after heat treatment in cadmium vapour
16	670.0	1.849		in crystals of series 2



centres were investigated in GaP. In the case of GaP a particular line appeared in the absorption and luminescence spectra corresponding to each of the distances between pairs of nitrogen atoms in the exciton complexes [11]. The heat treatment of  $\text{CdP}_2$  crystals in vacuum decreases the intensity of the higher-energy wing in the spectrum caused by nitrogen-pair centres ( $\text{N}^{\text{N}}$ ), while that of the low-energy wing increases. This may be explained as due to a decrease in the concentration of the nitrogen atom associates. Hence, the spectrum in the region 2.00 to 2.08 eV may be explained as the result of radiative recombination at nitrogen-exciton complexes, where the formation of associates of nitrogen pairs ( $\text{N}^{\text{N}}$ ) had occurred. When the temperature is above 120 K, the fine structure disappears completely and only the band on the short-wave wing (Fig. 2, curve 2) coinciding with the position of the spectrum related to the exciton-impurity complexes, exists. This result illustrates the superposition of spectra of different origins (Fig. 2).

The doublet having components 2.096 and 2.093 eV was systematically observed in crystals having p-type conductivity. It seems that this doublet is caused by the radiative recombination of exciton complexes localized at neutral acceptors. However, we cannot exclude the possibility that this doublet may be formed owing to crystal field splitting. The relationship between the luminescence intensity and temperature at constant level of excitation for this band is shown in Fig. 1 c. It is a linear relationship with an activation energy equal to 0.06 eV.

In the samples of crystals annealed in saturated cadmium vapour (Fig. 1 b, curve 2) the doublet vanishes and a single peak with maximum at 2.095 eV appears. Inversion of conductivity takes place after annealing in saturated cadmium vapour (from p-type to n-type), where the concentration of conducting electrons increases in direct proportion to the pressure of the cadmium vapour in which annealing takes place. In this case the concentration of cadmium vacancies in the crystal lattice either decreased or totally vanished and some of the cadmium atoms are found at interstitial positions. Therefore, it may be proposed that the band at 2.095 eV is caused by the recombination of excitons bound to neutral donors, which is in analogy with n-type GaAs [11]. This band was observed in all the samples of n-type  $\text{CdP}_2$  investigated by us. Simultaneously a new band without fine structure appears with maximum at 1.72 eV. Its intensity is directly proportional to the degree of saturation of the crystal with cadmium vapour. Furthermore, a band with maximum at 0.45 eV is detected in the absorption spectrum of n-type  $\text{CdP}_2$  [9]. It is possible to attribute the above band to the presence of interstitial cadmium atoms that create a donor level situated approximately 0.45 eV below the conduction band. This gives rise to channels of radiative recombination between donor and valence band.

The red band with maximum at 1.82 eV is present only in crystals prepared from less pure components and is caused by the recombination at complexes of twice ionized cadmium vacancies and singly ionized donors.

In order to confirm the idea that nitrogen centres take part in radiative recombination in  $\text{CdP}_2$ , the effect of doping  $\text{CdP}_2$  with two typical elements isoelectronic to phosphorus, As and Bi, is considered.

Fig. 3, curves a to c show the short-wave region of the cathodoluminescence spectrum at 6 K for  $\text{CdP}_2$  monocrystals undoped and doped with As and Bi, respectively. In Fig. 3, curve a and c the fine structure is present, while in Fig. 3, curve b it disappears and the intensity of luminescence is strongly decreased (by a factor approximately equal to 30). This may be explained by taking into consideration the appreciable increase in p-type conductivity ( $10^3$  to  $10^4$  times) and also the considerable compensation ( $(N_p - N_d)/N_p = 0.35$ ) that takes place in the  $\text{CdP}_2$  crystal after doping with arsenic. The total increase in the p-type conductivity may be attributed partly

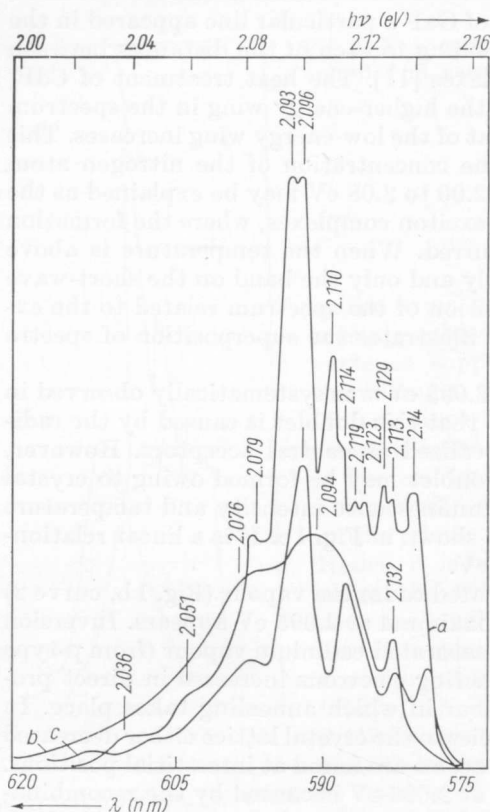


Fig. 3. The radiative recombination spectrum of  $\text{CdP}_2$  crystals at 6 K. (a) initial sample, (b) doped with As, (c) doped with Bi

to the acceptor levels due to arsenic atoms in the crystal lattice of  $\text{CdP}_2$  and partly to the filling of the phosphorus vacancies (acting as donors) by arsenic atoms [13]. This may be explained by the almost equal values of tetrahedral radii of arsenic and phosphorus. Hence there is a strong competition between arsenic and nitrogen atoms in replacing phosphorus atoms and also in filling their vacancies in the crystal lattice of  $\text{CdP}_2$ , as a result of which the fine structure in the high-energy wing (2.02 to 2.14 eV) disappears (Fig. 3, curve b).

In the case of bismuth the fine structure in the band (2.02 to 2.14 eV) is more or less retained, while its intensity is decreased by a factor of about three as compared to the luminescence intensity of the undoped single crystals of  $\text{CdP}_2$ . There is inversion of conductivity (from p-type to n-type) when  $\text{CdP}_2$  is doped with higher concentrations (about 1 wt%) of bismuth [13].

This can also be explained in terms of the tetrahedral radii of bismuth, cadmium, and phosphorus. The tetrahedral radii of cadmium and bismuth are almost equal, while that of phosphorus is much smaller than that of bismuth. Therefore, the bismuth atoms fill rather the vacancies of cadmium atoms than those of phosphorus. Cadmium vacancies act as acceptors in  $\text{CdP}_2$ . Hence decrease in p-type conductivity or inversion of conductivity type takes place in the case of higher concentrations of bismuth in  $\text{CdP}_2$ . The fine structure is retained since the bismuth atoms cannot fill the phosphorus vacancies or replace phosphorus atoms in  $\text{CdP}_2$ , hence bismuth atoms do not compete with nitrogen atoms in filling phosphorus vacancies or replacing phosphorus atoms.

#### 4. Summary and Conclusion

We have investigated samples of  $\text{CdP}_2$  undoped, annealed in vacuum and in saturated cadmium vapour, and doped with elements isovalent to phosphorus, As and Bi, respectively. The intensity in the region 2.02 to 2.14 eV varies with the nitrogen concentration in the various samples of  $\text{CdP}_2$  monocrystals investigated by us. Doping  $\text{CdP}_2$  monocrystals with elements isovalent to phosphorus, namely As and Bi, showed

that As competes with nitrogen in filling the phosphorus vacancies and also in replacing them, while Bi fills cadmium vacancies and replaces them in the crystal lattice of  $\text{CdB}_2$ .

We have established that radiative recombination in  $\text{CdP}_2$  takes place with the participation of exciton complexes localized at neutral acceptors and donors (cf. Table 1), exhibiting p-type and n-type conductivity, respectively, the type of conductivity being the result of natural defects or the introduction of dopants. It can be concluded that the uncontrolled impurity nitrogen in  $\text{CdP}_2$  gives rise to a region of luminescence in the higher-energy band 2.02 to 2.14 eV the details of which are tabulated.

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