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Cathodoluminescence of Cadmium Diphosphide Crystals under Uniaxial Deformation

By

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Cathodoluminescence spectra of CdP_2 crystals are studied at 6 K. The spectra are excited by a pulsed beam of electrons under uniaxial deformation of the samples. It is established that the creation of tension in the a and c directions leads to a shift of all band maxima of the spectral short-wavelength range to the low-energy and high-energy region. This is explained by a proportional change in the forbidden bandwidth induced by deformation. Variations in the intensity of certain sites of the radiation spectrum under crystal deformation as well as the investigation of temperature dependences of bands make it possible to explain their nature. The 2.142 eV line is associated with recombination of free excitons and the 2.132 and 2.110 eV bands are induced by recombination of excitons which are localized on isolated and nitrogen pair centres, respectively. Excitons which are localized on neutral acceptors and produced by intrinsic defects are responsible for the radiation with maximum of 2.097 eV.

Исследованы спектры катодолюминесценции кристаллов CdP_2 при 6 K, возбужденных пульсирующим пучком электронов при одноосной деформации образцов. Установлено, что при создании напряжения в направлениях a и c максимумы всех полос коротковолнового участка спектра смещаются соответственно в низкоэнергетическую и высокоэнергетическую область. Это обьясняется пропорциональным изменением ширины запрещенной зоны за счет деформации. Изменение интенсивности отдельных участков спектра излучения при деформации кристаллов, а ткаже исследования температурных зависимостей полос, позволило объяснить их природу. Линия 2,142 eV связывается с рекомбинацией свободного экситона, а полосы 2,132 и 2,110 eV обусловлены рекомбинацией экситонов локализованных соответственно на изолированных и парных азотных центрах. За излучение с максимумом 2,097 eV ответственны экситоны, локализированные на нейтральных акцепторах, создаваемые собственными дефектами.

1. Introduction

More than a dozen of works devoted to studies on the radiative recombination of cadmium diphosphide crystals are available in literature. However, the nature of luminescence centres in all of them is explained insufficiently, though the spectral structure in most investigations practically coincides. The first attempts to explain the nature of the radiative recombination centres were made by [1]. A model of possible electron transitions causing the radiation is suggested in [2]. Certain corrections in the energy band structure of cadmium diphosphide crystals were carried out on its basis. Since the crystals under study have a tetragonal structure and at the same time possess anisotropy $c/a = 3.73$ [3], it is expedient to study the radiation spectra under uniaxial

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deformation along the directions a and c in order to specify problems concerning the nature of "edge" luminescence. The cathodoluminescence spectra of CdP_2 and ZnP_2 under conditions of uniaxial compression are given in [4]. However, the authors do not discuss the nature of the spectral radiation bands. It has been established that in cadmium diphosphide crystals a tetragonal splitting of the valence band maximum occurs which is formed by a pair of almost degenerated subbands $\Gamma_7 + \Gamma_6$ (Γ_7 being the upper subband) and the gap between them is 47 meV. Basing on the analysis of the crystal structure and investigations of electron diffraction as well as on studies conducted by electron microscopy the authors of [5] were able to conclude about the existence of tetragonal cadmium diphosphide in different phases. This fact makes the interpretation of radiation spectra under crystal deformation more complicated. The purpose of this paper is to study the nature of the radiative recombination centres in CdP_2 being responsible for light emission in the short-wavelength region.

2. Experimental Method

30″-oriented samples of single crystals of the tetragonal modification having the specific resistance 10^9 to $10^{10}\ \Omega$ cm were used for the studies. The faces of cut parallelepipeds of $2 \times 2 \times 3$ mm³ size coincided with the main crystallographic planes (100), (010), and (001). The cathodoluminescence spectra (CL) are recorded at the temperature of liquid helium on the device described in [6]. The current density of the electron excitation beam was $(0.1$ to $1.0) \times 10^4$ A/m², duration of the pulse 300 ns (mean electron energy 40 keV). A standard equipment was added to the measuring device for creating uniaxial tensions.

3. Experimental Results and Discussion

The CL spectra without tensions do not differ in their structure from the spectra given in [1]. There are insignificant differences in the values of band maxima energies (within 2 meV). This is explained by the fact that contrary to [1] we have excited and recorded the radiation on oriented crystal faces. It is known that crystalline anisotropy suggests anisotropy of recombination radiation, that was observed in the experiment. The chosen orientation of the sample and its position in the device have resulted in certain shifts in the band maxima. Only four bands which are observed against a background of the whole spectrum were investigated. It was difficult to investigate other spectral lines because of the shift and mutual overlapping of the bands as well as because of the redistribution of their intensities under the effect of deformations. When the tension is created along the directions a and c the maxima of all bands of CL spectra shift to the low-energy and high-energy regions, respectively (Fig. 1). The basic parameters of the studied bands are presented in Table 1.

As is seen, almost all bands have different coefficients $\Delta E/\Delta T$, $\Delta E/\Delta P$, that evidences a different nature of the centres which evoke this radiation. In [6] the band having the maximum at ≈ 2.142 eV is associated with the recombination of free excitons, and all other spectra in the "edge" region are explained by the radiative recombination of exciton–impurity complexes and their phonon replicas. Under uniaxial compression the shift of band maxima is characterized by a linear dependence (Fig. 2) and with rising temperature (without external uniaxial pressure) no linearity is observed (Fig. 3).

An increase in deformation along c results in a shift of the band maxima towards the high-energy region, that is quite natural for the case of a decrease in lattice parameters. This leads to a rise of the energy of both free exciton and exciton–impurity
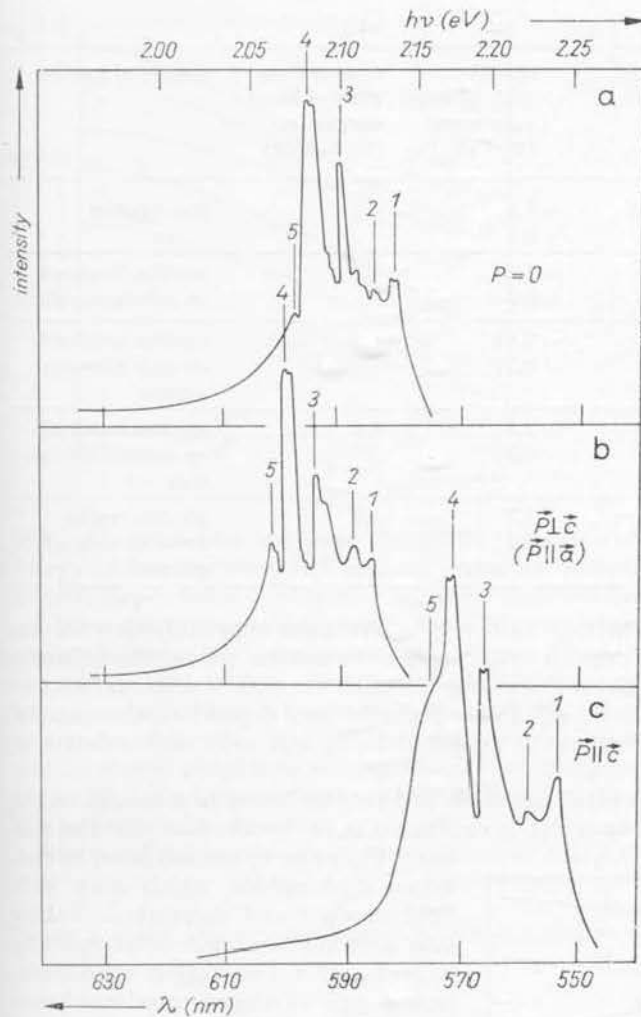
Fig. 1. Cathodoluminescence spectra of CdP₂ crystals at 6 K a) without deformation; b) with deformation of 100 MPa, *P* || *c*; c) under uniaxial compression of 100 MPa, *P* || *c*

complexes. A similar situation is observed at lowering the sample temperature, though the law of the band shift is to some extent different. As suggested in [7], the temperature shift of the gap width in a certain approximation may be represented in the form

$$E_g(T) = E_g(0\ \mathrm{K}) - \alpha\,\frac{T^2}{T + \theta},$$

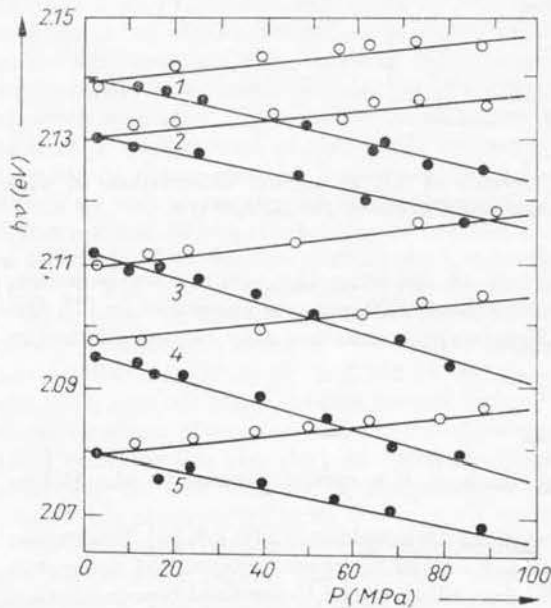where α is an experimentally chosen coefficient, θ a constant close to the Debye temperature.

The Debye temperature at 100 K for cadmium diphosphide is 210.7 K [6]. The values of these parameters ($\alpha = 7 \times 10^{-4}$ eV/K; $\theta = 210$ K) were determined from the temperature shift of the band at 2.142 eV. According to the theoretical representation

Table 1

No.	energy of band maximum (eV)	direction of compression	specific shift of band maximum (10^{-9} eV/Pa)	temperature shift of band maximum (10^{-4} eV/K)	nature of bands
1	2.142	$P \parallel a$ $P \parallel c$	-1.8 $+0.8$	4.7	free exciton
2	2.132	$P \parallel a$ $P \parallel c$	-1.8 $+0.7$	4.3	exciton localized on nitrogen centres
3	2.110	$P \parallel a$ $P \parallel c$	-2.44 $+0.77$	4.2	exciton localized on pair nitrogen centres
4	2.097	$P \parallel a$ $P \parallel c$	-2.1 $+0.5$	4.6	exciton localized on neutral acceptors
5	2.08	$P \parallel a$ $P \parallel c$	-1.7 $+0.8$	4.3	photon replica $h\nu - 52$ meV of phonon

of the hydrogen-like model of excitons in the effective mass approximation the exciton binding energy does not depend on crystal deformation unless the effective masses depend on pressure [8]. Since the energy of band maxima is a linear function of pressure, i.e. $dh\nu_{max}/dP = $ const, m_e^* and m_n^* should not depend on the uniaxial pressure. In this case the disperse curves do not deform, but only shift relative to another.

As seen the energy shift of spectral bands should be attributed to a change in the gap width. The increase in the gap width is explained in [4] by the fact that the subband Γ_5 is the upper subband in cadmium diphosphide which may shift both upward and downward. Taking into account the spin–orbit splitting in terms of a two-valued representation a pair of degenerated subbands $\Gamma_7 + \Gamma_6$ should be considered instead

Fig. 2. Dependence of energy shift of radiation shift on applied uniaxial tension $P \perp c$ (●), $P \parallel c$ (○). For explanation of the curve numbers see Table 1
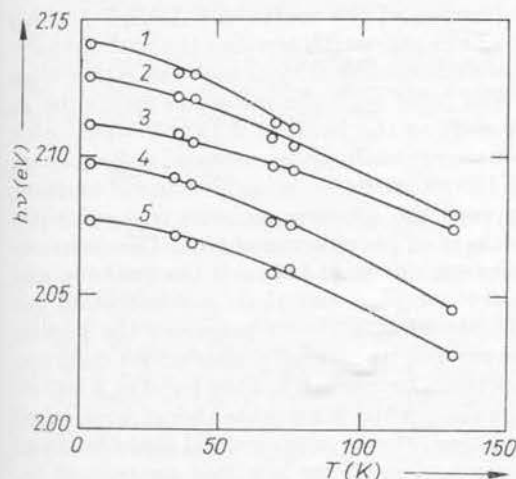
Fig. 3. Shift of the radiation band maxima with temperature variation; (1) to (5) see Table 1

of Γ_5. In connection with the change in the gap width of a crystal the values of the energy of free excitons and exciton–impurity complexes change as well. In this case a linear dependence is observed between their changes.

Under compression along a it is most natural to suppose that the distance between atoms decreases and, consequently, the gap width increases and so do the values of the energy both of free exciton and exciton–impurity complexes. However, judging from the shift of bands responsible for their recombination, the values of their energy, vice versa, decrease. Having analyzed the crystal structure of cadmium disulphide and its elastic properties we concluded that compression along a leads to an increase of the distance between atoms along c, being more considerable than the decrease in the perpendicular direction.

The relative growth of sample dimensions along c is equal to

$$\varepsilon' = \mu\varepsilon ,$$

where μ is the Poisson coefficient which is equal to 0.35 for CdP_2 [9],

$$\varepsilon' = \frac{\Delta c}{c}, \qquad \varepsilon = \frac{\Delta a}{a} .$$

Taking into account that compression created under uniaxial deformation in the experiments follows Hooke's law $p = \varepsilon E$, and $E_{100} = 5.66 \times 10^{10}$ Pa, $E_{001} = 6.78 \times 10^{10}$ Pa [9], it is possible to establish that c rises with the decrease of a by about Δa. The presence of anisotropy of both crystal structure and elastic constants leads to the fact that under compression along a the growth of Δc is 1.3 times higher than the decrease of Δa. The initial lattice parameters are as follows: $a = 0.5283$ nm, $c = 1.9808$ nm [10]. In this case the distance between phosphorus chains parallel to the plane (001) will grow. The chemical bond in cadmium disulphide is stronger inside the layer packet than the interpacket interaction [4, 5]. Uniaxial deformation of the sample along c will lead to a decrease of the distance between phosphorus atoms. According to the data of [1] the replacement of nitrogen in the cadmium disphosphide crystal lattice by phosphorus atoms is of isoelectronic character. The band at 2.133 eV was associated with the recombination of excitons localized on isolated nitrogen centres. According to the data of the authors the specific shift of the band at 2.133 eV correlated well with the shift of the free exciton line at 2.142 eV

under uniaxial pressure along a and c. A decrease of the coefficient $\Delta E/\Delta T$ for this band as compared to the temperature shift of the gap width testifies the fact that the band is associated with recombination of the exciton–impurity complexes rather than being the phonon replica of the first line. The band with the radiation maximum at 2.110 eV has the same value of the energy shift as the band at 2.132 eV with rising temperature. However, it possesses a higher energy shift under uniaxial deformation. There are reasons to associate the band at 2.110 eV with the recombination of excitons localized on nitrogen pair centres. In this case the nitrogen pair centres evidently form between nitrogen atoms in parallel packets of phosphorus chains. The deformation perpendicular to the axis c will increase the distance between the packets, and thus the energy of such an exciton–impurity complex and their concentration per volume unit will decrease more intensely. The band at 2.110 eV possesses the highest specific energy shift of the radiation maximum and its intensity rises under deformation along c, that confirms the above assumption. The intensity of the band at 2.097 eV under compression along c increases considerably, while it remains almost unchanged under deformation in the perpendicular direction. It was supposed [1] that this band for p-type crystals is caused by recombination of excitons localized on neutral acceptors.

The band at 2.097 is the most intensive one against the background of the entire spectrum, that may evidence a comparatively high concentration mainly of neutral acceptors. Most probably intrinsic defects may play their role. It is known that in cadmium diphosphide among intrinsic defects cadmium vacancies and complexes formed on their basis are acceptors [11]. The deformation of the unit cell (at $P \parallel c - C_{33}$) is determined by the relative shifts of atoms inside the cell which being proportional to the load differ essentially in CdP_2 for various atoms, since the interaction between phosphorus chains perpendicular to c is $\approx 10^4$ to 10^5 times weaker than intrinsic interactions [14]. Most likely that deformation along c really increases the concentration of cadmium vacancies in the unit volume and, consequently, the concentration of excitons localized on these defects as well. In addition, the relative intensity of the band in the spectrum and its half-width varied in the samples obtained from different technological batches and increased noticeably in the samples with a higher concentration of holes. An increase in specific conductivity in p-type CdP_2 crystals may be provided in the first place by the growth of the acceptor-type centres V_{Cd}.

Thus it is possible to conclude that the band with the maximum at 2.097 eV is associated with recombination of excitons localized on neutral acceptors, cadmium vacancies playing a role. The splitting of the band is observed not on all samples. The presence of different polytype modifications in the crystal may lead to a smearing of the spectral structure, since a distortion of periodicity in the direction perpendicular to the layers causes the disturbance of the optical selection rules by the wave vector, and this leads to the band broadening [12]. The equivalent location of cadmium sites in the lattice of tetragonal cadmium diphosphide does not cause the splitting.

The wide radiation band with the maximum at 2.08 eV is the phonon replica of the band at 2.132 eV with phonon energy of 52 meV. These lines have approximately equal values of the coefficients $\Delta E/\Delta T$ and $\Delta E/\Delta P$, that indicates the same nature of the radiative recombination centres responsible for this radiation. Having studied the Raman spectrum the authors of [13] give the value of the phonon energy in CdP_2 equal to 51.5 meV. A certain discrepancy of phonon energy values may be explained by the inaccuracy in determining the band maximum resulting from the presence of other bands in the long-wavelength region whose separation is not possible. This leads to the formation of the long-wavelength "tail" consisting of several mutually

overlapping bands being phonon replicas of the studied short-wavelength region of the spectrum.

Thus, radiation in cadmium diphosphide crystals is caused by recombination of free excitons and exciton–impurity complexes where nitrogen and intrinsic defects play the role of impurities.

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