
INTERLAYER EXCITONS: EXPERIMENT AND THEORY**M.P.LISITSA, F.V.MOTSNYI, O.S.ZINETS**UDC 535.346; 535.341
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Optical properties of 2H-PbI₂ single crystals intercalated by hydrazine molecules (N₂H₄) have been studied. Significant (more than 30 times) amplification of the polariton emission from the upper polariton branch with following quenching under increasing the concentration of hydrazine molecules in interlayer spaces has been found out. That is caused by the transitions of polaritons of the lower branch into polaritons of the upper branch by scattering at hydrazine molecule inclusions. The highly stable polytype transition 2H-4H has been registered which is caused by the formation of “covalent bridges” by interlayer hydrazine molecules with the neighbouring layer sandwiches. The new type of excitons — so-called interlayer excitons (the excitons localized in the interlayer space at incorporated molecules (atoms)) has been found which cause the appearance of a new doublet (4928 Å, 4934 Å) in the photoluminescence spectra between the exciton lines $n = 1$ and $n = 2$. A simple model for interlayer excitons was considered which takes into account the peculiarities of chemical bonding and polytype properties of such single crystals as 2H-PbI₂.

Introduction

Anisotropy of crystal lattices and phenomena related to it have been studied for a long time. A number of effects exist whose appearance is indeed a consequence of the crystal lattice anisotropy. Among them are piezoelectric phenomena, double-beam refraction, dichroism, etc.

The tremendous class of layered substances also belongs to anisotropic compounds. They differ from the well-studied traditional ones by a high anisotropy of chemical bonding caused by the strong ion-covalent binding in separate layer sandwiches and weak Van der Waals binding between neighbouring sandwiches. Owing to the lattice construction peculiarities, impurity atoms and molecules can be incorporated into the Van der Waals space. This phenomenon was found in [1] and named intercalation. The interest to the intercalation

phenomenon is connected to the search for new physical effects and possibilities of the exciton mechanism for realization of high temperature superconductivity [2–4], investigation of low-dimensional effects and physical processes at the boundary of different media, development of supercapacitors and chemical current sources. Using intercalated single crystals, Lisitsa, Motsnyi and Sergeev [5] found, in particular, a new type of excitons named interlayer excitons. Interlayer excitons are those localized in the interlayer space on incorporated molecules (atoms). It should be noted that the formation of these excitons is possible just in layered substances. They can be considered, in some cases, by analogy with the Davydov splitting.

The present paper deals with the experimental and theoretical studies of interlayer excitons. The results of investigation of reflection, photoluminescence (PL) and Raman scattering spectra of 2H polytype PbI₂ layered single crystals intercalated by hydrazine (N₂H₄) molecules are discussed on this basis.

1. Samples and Intercalation Method

Intercalated samples were usually powders or films. Therefore, it was necessary to select initial samples for intercalation and develop a method for obtaining intercalated ones of sufficiently big sizes. To this end, we used Bridgman-grown 2H-PbI₂ layered single crystals. These are convenient compounds for intercalation because of their high quantum yield of PL in the exciton region [6-8], as well as low hardness, small rigidity along layers, and existence of a large (up to 30) number of polytypes.

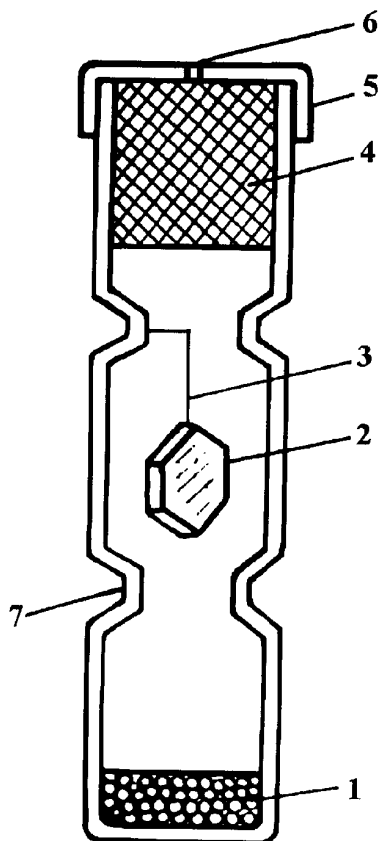


Fig. 1. Chamber for intercalation. 1 — mixture N_2H_4+BaO , 2 — PbI_2 sample, 3 — glass thread, 4 — dryer, 5 — plug, 6 — outlet, 7 — contractor

As an intercalant, we used dehydrated hydrazine because of its high ability to penetrate into the interlayer space and create a stable compound with the crystal matrix [9]. It should be indicated that hydrazine without water is more explosive than nitroglycerin. Therefore, the intercalated samples were obtained in a special chamber developed by Dr.A.Melezhyk in our laboratory (Fig.1). It insures safety and excludes water penetration into the crystal lattice. A glass tube with three compartments was filled with dry air. In the lower part, mixture 1 of hydrazine obtained by the technique described in [10] and barium oxide (BaO) was placed to insure absorption of residual water. In the middle part of the tube, crystal 2 was hanged up with a glass thread 3. The upper part of the chamber was isolated from the medium using a dryer containing KOH or BaO . The chamber was shut by plug 5 with outlet 6 to reduce the excess pressure. Intercalation was carried out in the following way. Hydrazine vapour diffused slowly through contractor 7 and was absorbed by the sample. The pro-

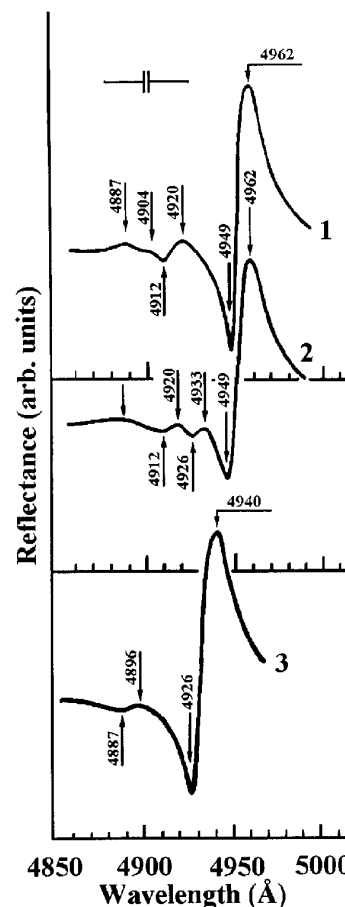


Fig. 2. Exciton reflection spectra of initial $2H-PbI_2$ single crystals (1) and those intercalated with small (2) and high (3) hydrazine concentrations at $T=4.2$ K and $\vec{E} \perp \vec{C}$

cess was controlled by observing a change in the sample colour.

A new chamber was also built up which enabled us to get intercalated single crystals with a definite concentration of hydrazine using the technique of precise weighting.

2. Results and Discussion

Exciton reflection and photoluminescence spectra of the surface as-cleaved in air were measured using a specially designed setup with high resolution on the base of a spectrograph PGS-2 (7.2 \AA/mm) and a spectrometer DFS-24 (4.5 \AA/mm), a pulse transformer UPI-4 and, if needed, a pulse photometer IPF-2. Wavelengths of a tunable argon laser LG106-1 were controlled by a monochromator UM-2. Temperature was stabilized with accuracy better than 0.1%. So, the experimental setup

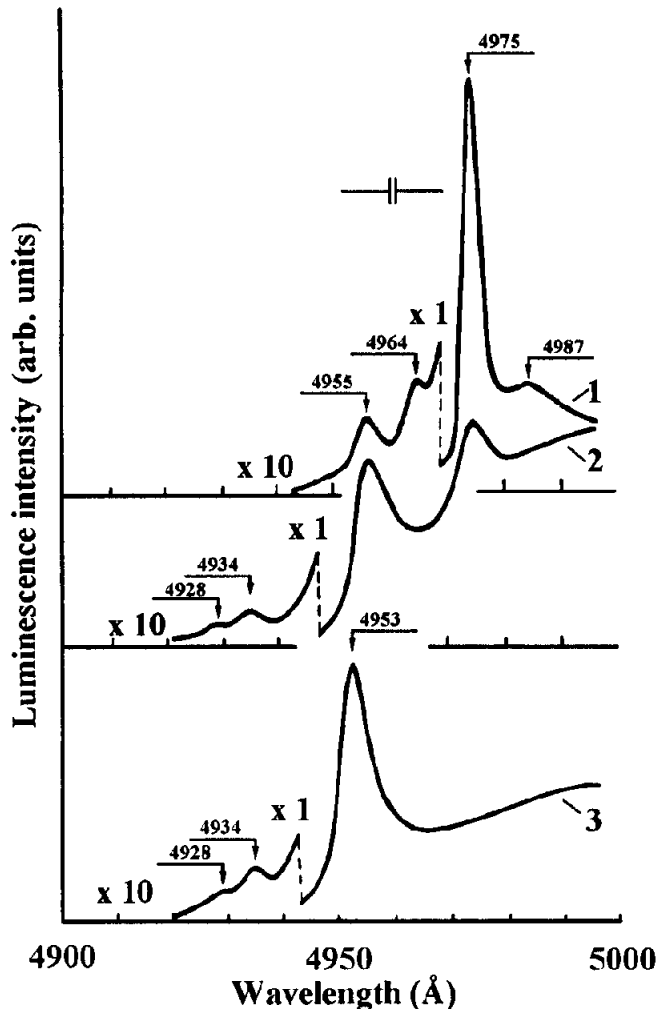


Fig. 3. Exciton photoluminescence spectra of initial 2H-PbI₂ single crystals (1) and those intercalated with small (2) and high (3) hydrazine concentrations. $T=4.2$ K., $\lambda_{\text{excit}}=4880$ Å

was highly sensitive and had high spectral resolution ability.

Typical exciton reflection spectra of initial (curve 1) and intercalated with hydrazine (curves 2, 3) 2H-PbI₂ single crystals are presented in Fig. 2. One can see that, for the sample with a low hydrazine content, new oscillations with extrema at 4926 and 4933 Å were clearly observed between the exciton bands $n = 1$ and $n = 2$. At a larger hydrazine concentration (curve 3), the excitonic bands shift to the high-energy side by about 10.7 meV and the minima of the exciton oscillation $n = 1$ and new oscillation coincide. The maximum of the new oscillation was not observed, and the band halfwidth increases from 6.5 to 7.1 meV.

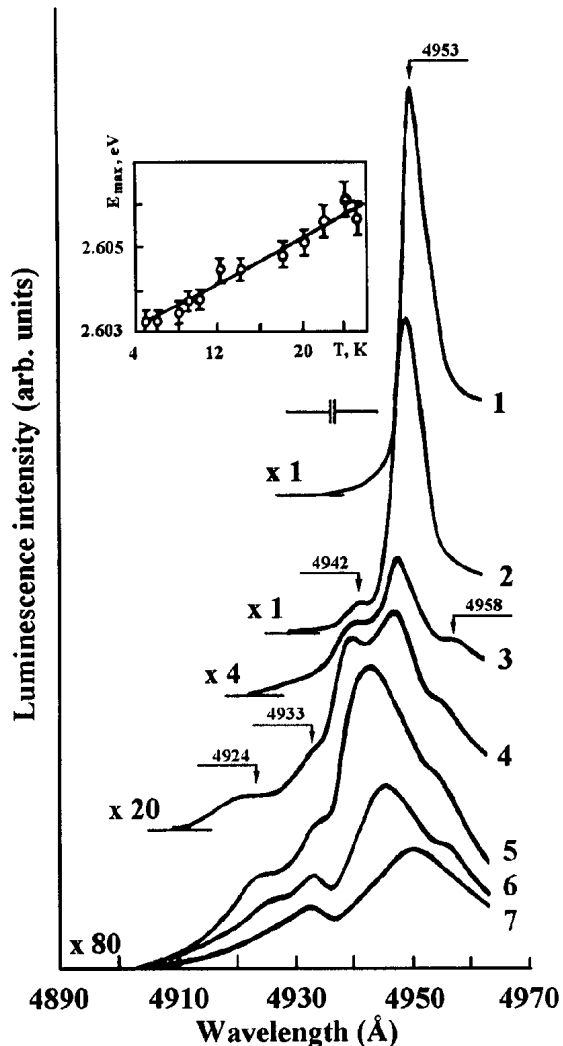


Fig. 4. Influence of temperature on photoluminescence spectra of 2H-PbI₂ single crystals intercalated with small hydrazine concentration. T , K: 1 - 5, 2 - 10, 3 - 20, 4 - 25, 5 - 35, 6 - 45, 7 - 55. Insert: the dependence of the energy position of the maximum photoluminescence of line 4953 Å on the temperature, $\lambda_{\text{excit}} = 4880$ Å

Exciton photoluminescence spectra of the same samples at 4.2 K are shown in Fig. 3. It is seen that, in intercalated crystals, the intensity of the line of the exciton bound to neutral donors (4975 Å) is about two times lower and the emission intensity from the upper polariton branch (4955 Å) is more than thirty times higher. At the same time, the emission line from the lower polariton branch (4964 Å) and the exciton+phonon line were not observed. Also a new weak doublet (4928, 4933 Å) appears with a more intense longwave component in the region of the new

oscillation. The doublet energies and the intensity ratio are independent of the intercalant content. After quenching the line of the exciton bound to a neutral donor, an increase in the intensity of the new doublet and the appearance of an additional line (4953 Å) with increase in the hydrazine concentration were observed. Influence of temperature on the photoluminescence spectra of intercalated PbI₂ in the range from 4.2 to 55 K is illustrated in Fig. 4. It was found that (1) the intensity varies between lines 4953 and 4942 Å and both lines shift to the short wavelength side, with the temperature coefficient $dE/dT = 1.5 \cdot 10^{-4}$ eV/K, (2) the new doublet energies and the intensity ratio of the doublet components are independent of temperature.

The observed increase in the emission from the upper polariton branch was previously predicted theoretically by Sugakov [11, 12]. This phenomenon is known today as the Sugakov one. The reason for the Sugakov phenomenon is scattering of polaritons of the lower polariton branch by various defects of a crystal lattice due to the transformation of a lower branch polariton into a polariton of the upper branch. It was analyzed in detail by Sugakov and Kryuchenko [13] who considered the scattering of electromagnetic waves in dispersive media by inclusions. The theory gives that the intensity of photoluminescence with p or s polarization into angle θ for the inclusion concentration distribution by size $N(R)$ is determined by the sum of the scattering intensities of single inclusions. At first, the intensity increases with the inclusion radius as R^3 and then decreases as R^{-1} . Hence, the enlarging of inclusions, their total volume being constant, should lead to the quenching of the emission from the upper polariton branch. This is in agreement with experimental data. With increase in the hydrazine concentration, an intense line 4953 Å was observed in the longitudinal exciton region in 2H-PbI₂. Excitonic spectra of reflection and photoluminescence of intercalated samples with higher hydrazine concentration coincide with spectra of 4H-PbI₂ polytype [14, 15] whose lattice constant is two times larger than that of 2H-PbI₂ polytype [16]. The line 4953 Å can be assigned to an exciton bound to lattice defects [14]. This is proved by the temperature quenching of this line (decrease in the exciton impurity complex concentration) which is accompanied with the intensity increase of the free exciton line 4942 Å (increasing the free exciton concentration), as well as a shortwave shift of both lines with increase of temperature from 4.2 to 30 K, that reflects the band gap dependence of 4H polytype on temperature.

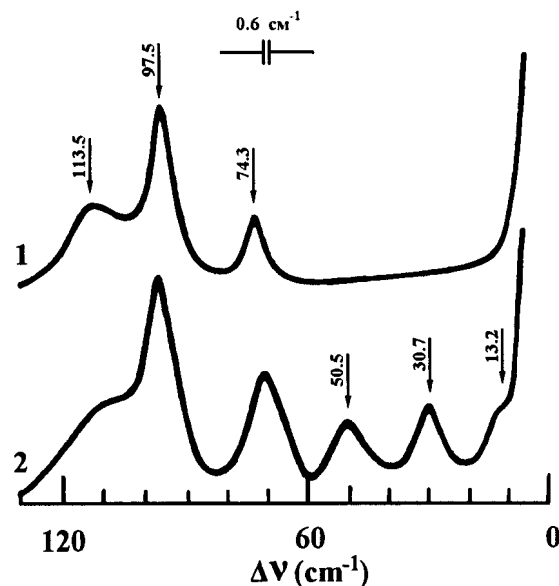


Fig. 5. Raman spectra of initial 2H-PbI₂ single crystals (1) and those intercalated with small hydrazine concentration (2) at $T=300$ K, $\lambda_{\text{excit}}=6328$ Å

Thus, the increase of the emission intensity from the upper polariton branch with the hydrazine concentration in 2H-PbI₂ crystals and the next quenching are described satisfactorily by the theory.

The new doublet (4928, 4934 Å) between the exciton states $n = 1$ and $n = 2$ in 2H polytype corresponds to quasi-surface excitons previously observed in layered BiI₃ crystals with an atomically pure surface [17]. However, in contrast to the BiI₃ case, the doublet is observed in intercalated crystals with a real surface and corresponds to excitons bound to hydrazine inclusions in interlayer spaces. On the other hand, the appearance of a doublet with characteristic intensity distribution between components (the long wavelength component is about two times more intense than the short wavelength one in the spectra of both polytypes) indicates the presence of two translationally nonequivalent positions of N₂H₄ molecules in the lattice. Thus, the inclusion of hydrazine into the 2H-PbI₂ lattice, even in a small quantity, should be accompanied by the creation of an embryo of 4H polytype which have two molecules PbI₂ in the unit cell and there are two non-equivalent layers. This assumption is proved by studies of the Raman spectra of initial sample (curve 1) and one intercalated with small concentration of hydrazine (curve 2) (Fig. 5).

additional lines in optical spectra. Some lines and bands in reflection and photoluminescence spectra studied in the previous section may be assigned to localized excitons at intercalated molecules in layered crystals.

One may assume that, in a layered crystal with ionic or covalent bonding in layers and Van der Waals interaction between layers, the excitons behave like the Wannier–Mott excitons in the layer plane and move as the Frenkel excitons between layers. Using the standard method in approximation of the nearest interacting layers, the exciton energy in a perfect crystal can be written as

$$E = E_g + \frac{\hbar^2 k_{\perp}^2}{2m_{\perp}} - \frac{E_{\text{ex}}}{(n + \frac{1}{2})^2} + 2M \cos(ka), \quad (1)$$

where E_g is the energy gap, k_{\perp} , m are the wave vector and mass of a two-dimensional Wannier–Mott exciton; E_{ex} is the exciton Rydberg, a is the lattice constant along the optical axis, M is the resonance interaction energy in a perfect crystal,

$$M = \langle \phi_k^0 \phi_{k+1}^f | V_{k,k+1} | \phi_k^f \phi_{k+1}^0 \rangle, \quad (2)$$

ϕ_k^0 is the wave function of an unperturbed layer and ϕ_{k+1}^f is the wave function of a layer with a two-dimensional Wannier–Mott exciton. In the case where only two neighbouring layers are disturbed under intercalation, as shown in [10], a localized state with a wave function which exponentially decreases with the distance from the intercalated layer may exist. For the energy and radius of localization, the following expressions were obtained:

$$\Delta E = \frac{M\gamma^2}{1 + \gamma}, \quad r = \frac{a}{\ln(1 + \gamma)}, \quad (3)$$

where $\gamma = \frac{h + \delta M}{M}$, h is the difference in the exciton energies in the layer perturbed by intercalated molecules and a non-perturbed one; δM is the change in the resonance energy for the transition between the layers neighbouring to intercalated layers. Localization is possible under the condition $\gamma > 0$.

The absorption coefficient for a localized exciton in the case of a small intercalant concentration is of the following form:

$$\mu = \frac{4\pi^2 e^2}{m^2 n(\omega) c \omega} |(\epsilon p)_{0,i} \varphi(0)|^2 |\psi|^2 \delta(E^i - E^0 - \hbar\omega) N, \quad (4)$$

where

$$|\psi|^2 = \frac{2(1 - \exp(-2\kappa a))}{(1 - \exp(-\kappa a))^2}, \quad (5)$$

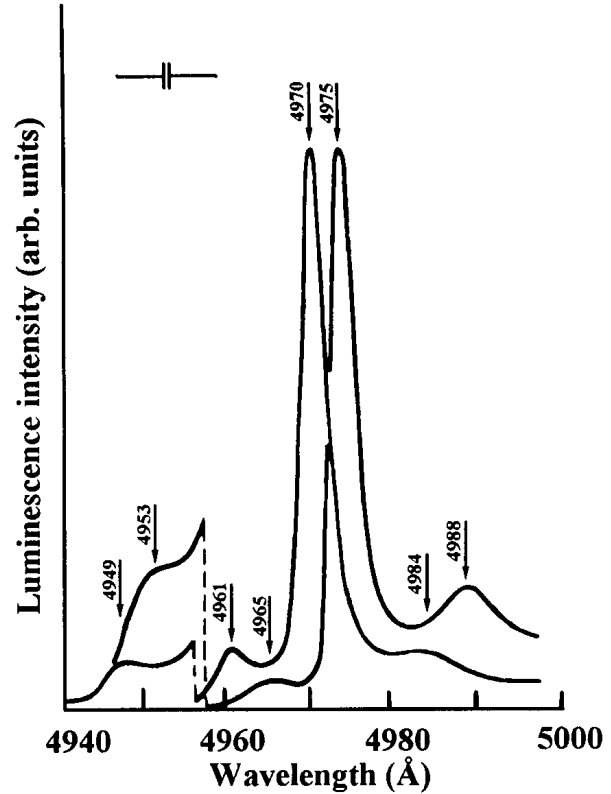


Fig. 8. Exciton photoluminescence spectra of the initial 2H-PbI₂ single crystal samples (1) and those on a scotch tape (2). $T=4.2$ K, $\lambda_{\text{excit}}=4880$ Å

N is the number of intercalated layers per unit length, α_i is the absorption coefficient for a single layer, $n(\omega)$ is the refractive index, \vec{e} is the light polarization vector, \vec{p} is the matrix element of the electron transition from the valence to conduction band at k_{\perp} of an electron and a hole in a two-dimensional exciton, E^0 and E^i are the energies of the ground and excited states of the crystal, and κ is the inverse localization radius. If, for instance, the values of γ and M are assumed to be equal to 0.1 and 0.1 eV, respectively, the localization radius will be about 10 Å and energy $\delta E = 1$ meV, that are in satisfactory agreement with the experimental data.

Conclusions

Optical properties of 2H-PbI₂ single crystals intercalated by hydrazine have been studied. Significant (more than 30 times) amplification of the polariton emission from the upper polariton branch has been found out and explained by transitions of the polaritons of the lower branch into the polaritons of the upper

branch by scattering by intercalated molecules. The highly stable polytype transition 2H-4H has been registered and explained by the formation of “covalent bridges” of interlayer hydrazine with the neighboring layer sandwiches. The new type of excitons, the so-called interlayer excitons (the excitons localized in the interlayer space at incorporated molecules (atoms)), has been found. They cause the appearance of a new doublet (4928, 4934 Å) in PL spectra between the exciton lines $n = 1$ and $n = 2$. A simple model for interlayer excitons was considered, taking into account the peculiarities of chemical bonding and polytype properties of such single crystals as 2H-PbI₂.

It is clear that the same effects can be observed in optical spectra of intercalated chain crystals.

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МІЖШАРОВІ ЕКСИТОНИ: ЕКСПЕРИМЕНТ І ТЕОРІЯ

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Резюме

Вивчено оптичні властивості шаруватих монокристалів 2H-PbI₂, інтеркальованих гідрaziном. Виявлено значне (більше ніж у 30 разів) підсилення інтенсивності поляризованого випромінювання з верхньої поляритонної вітки з наступним його гасінням при збільшенні концентрації гідразина в міжшаровому просторі, що викликане перетворенням поляритонів нижньої вітки в поляритони верхньої вітки за рахунок розсіювання на включеннях гідразина і яке визначається їхніми розмірами. Зареєстровано високостабільний структурний фазовий перехід 2H-4H, що зумовлений утворенням “ковалентних містків” молекулами гідразина із сусідніми шаровими пакетами. Виявлено новий тип екситонів — міжшарові екситони (екситони, що локалізовані на молекулах інтеркалянта), — які зумовлюють появу нового дублету в спектрах фотолюмінесценції між екситонними лініями $n=1$ і $n=2$. Запропоновано просту модель для міжшарових екситонів, яка враховує особливості хімічної будови і політипний склад таких монокристалів, як 2H-PbI₂.

МЕЖСЛОЙНЫЕ ЭКСИТОНЫ: ЭКСПЕРИМЕНТ И ТЕОРИЯ

М.П.Лисиця, Ф.В.Моцный, О.С.Зинець

Резюме

Изучены оптические свойства слоистых монокристаллов 2H-PbI₂, интеркальированных гидразином. Обнаружено значительное (более чем 30-кратное) усиление интенсивности поляризованного излучения с верхней поляритонной ветви с последующим гашением при увеличении содержания гидразина в межслойном пространстве, вызванное превращением поляритонов нижней ветви в поляритоны верхней ветви вследствие рассеяния на включениях гидразина и определяемое их размерами. Зарегистрирован высокостабильный структурный фазовый переход 2H-4H, обусловленный образованием “ковалентных мостиков” молекулами гидразина с соседними слоевыми пакетами. Обнаружен новый тип экситонов — межслойные экситоны (экситоны, локализованные в межслойном пространстве на молекулах интеркалянта), — обуславливающие появление нового дублета в спектрах фотолюминесценции между экситонными линиями $n=1$ и $n=2$. Предложена простая модель для межслойных экситонов, учитывающая особенности химического строения и политипные свойства таких монокристаллов, как 2H-PbI₂.