

Spectroscopy of ytterbium-doped InP under high hydrostatic pressure

A. Kaminska,¹ A. Kozanecki,¹ S. Trushkin,¹ and A. Suchocki^{1,2}

¹*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland*

²*Institute of Physics, Kazimierz Wielki University, Weysenhoffa 11, Bydgoszcz 85-072, Poland*

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The results of high-pressure low-temperature optical measurements in diamond-anvil cell of bulk indium phosphide crystals doped with Yb are reported. The observed initial increase in energy of f - f intrashell transitions between the $^2F_{5/2}$ excited and $^2F_{7/2}$ ground levels at pressure up to 6 GPa is interpreted as a result of a linear increase in the spin-orbit parameter of Yb³⁺ ions with pressure coefficient equal to 0.0059 cm⁻¹/GPa due to the covalency effects and mixing of the Yb³⁺ and phosphorus wave functions. Above 6 GPa the pressure dependences of the peak positions of all the luminescence lines flatten out and the values of pressure coefficients strongly decrease. A tentative explanation is provided in terms of the f levels of Yb³⁺ approaching of the top of the valence band of InP crystal host, which limits further increase in f - f intrashell transitions energies above 6 GPa pressure.

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I. INTRODUCTION

The intra- $4f$ -shell luminescence of rare-earth (RE) ions doped into semiconductor hosts has been attracting a keen interest due to their potential optoelectronic applications in electrically pumped light-emitting diodes or lasers as well as for fundamental studies.¹⁻⁴ Among the RE doped III-V semiconductors InP:Yb is one of the most intensively studied owing to its strong Yb-related luminescence at about 1 μ m. Although the energy-level scheme of Yb³⁺ in the InP crystal is quite well established^{1,5-8} and light-emitting p - n junction diodes have been realized in ytterbium-doped InP over 14 years ago,⁹ the ordering of the crystal-field levels is still a matter of discussion and the mechanism of energy transfer between the Yb $4f$ shell and InP host is still not fully comprehended.

As it has been verified by the studies of photoluminescence (PL) temperature dependence and photoluminescence excitation,⁷ electron-paramagnetic-resonance,^{5,6} and magneto-optical experiments⁸ the Yb ions doped into indium phosphide form one optically active center with a tetrahedral cubic T_d symmetry replacing indium on a substitutional site. The observed emission at about 1 μ m is due to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ intra- $4f$ -shell transition of Yb³⁺. Since the PL decay time of Yb³⁺ in InP is about two orders of magnitude shorter than that observed usually in ionic materials,¹⁰⁻¹³ Körber and Hangleiter¹⁴ concluded that it must be determined mainly by nonradiative Auger processes. Körber *et al.*¹⁵ has revealed that for ytterbium concentration larger than the residual donor concentration, the InP:Yb samples exhibit p -type conduction. It is in agreement with Hemstreet's predictions¹⁶ indicating that Yb introduces a shallow acceptor state in InP, corresponding to a Yb³⁺-Yb²⁺ transition. The charge-transfer transitions are crucial for understanding the influence of pressure on the energy structure of the Yb ions in InP and related compounds.

In this work we studied the influence of hydrostatic pressure on the luminescence spectra and radiative transition probabilities of the intra- $4f$ -shell transitions of Yb³⁺ ions in bulk InP crystals with use of a diamond-anvil cell (DAC)

technique. Pressure, like temperature, is a basic thermodynamic variable which is useful in studying the fundamental properties of materials and the DAC technique enables us to investigate their spectroscopic properties as well as phase transitions. The pressure effects in InP are especially interesting because of very close pressure values of the phase transition from the zinc blende to rock salt phase and the transition from the direct to indirect band gap. The phase transition was observed by different authors at pressures from 9 to 10.8 GPa,¹⁷⁻²⁰ whereas the direct to indirect band-gap transition—from 6 to 9 GPa, depending on the electron concentration of the sample.²¹⁻²³ The theoretical calculations of Bouarissa²⁴ and Gorczyca *et al.*²⁵ predict the direct band-gap to indirect band-gap transition to occur at pressures equal to 9.02 GPa or 10.4 GPa, respectively.

The paper is organized in the following way: in Sec. II we describe the investigated sample and the experimental methods. In Sec. III first results of spectroscopic studies of the InP:Yb crystal at ambient pressure and at different temperatures are reported in order to understand basic properties of the system. Then the high-pressure studies of f - f intrashell transitions of Yb³⁺ ions as well as the absorption edge of InP crystal host are presented, followed by the fit of the model and the discussion of results explaining the pressure dependence of the radiative transitions of the Yb dopant ions. Finally, a summary and conclusions are presented in Sec. IV.

II. EXPERIMENT

InP:Yb crystal used in these studies, revealing n -type conductivity, has been grown by a synthesized solute diffusion method.²⁶ Yb was added to the solution at the level of 0.1%. Continuous-wave emission spectra were obtained using the second harmonic of an YAG:Nd laser (532 nm) as an excitation source. The spectra were measured with the use of a GDM-1000 double-grating monochromator equipped with a cooled photomultiplier (EMI 9684B) with an S1-type cathode and an SR530 lock-in amplifier. The spectra were corrected for the quantum efficiency of the detection system. The high-pressure measurements up to 11.5 GPa (i.e., above

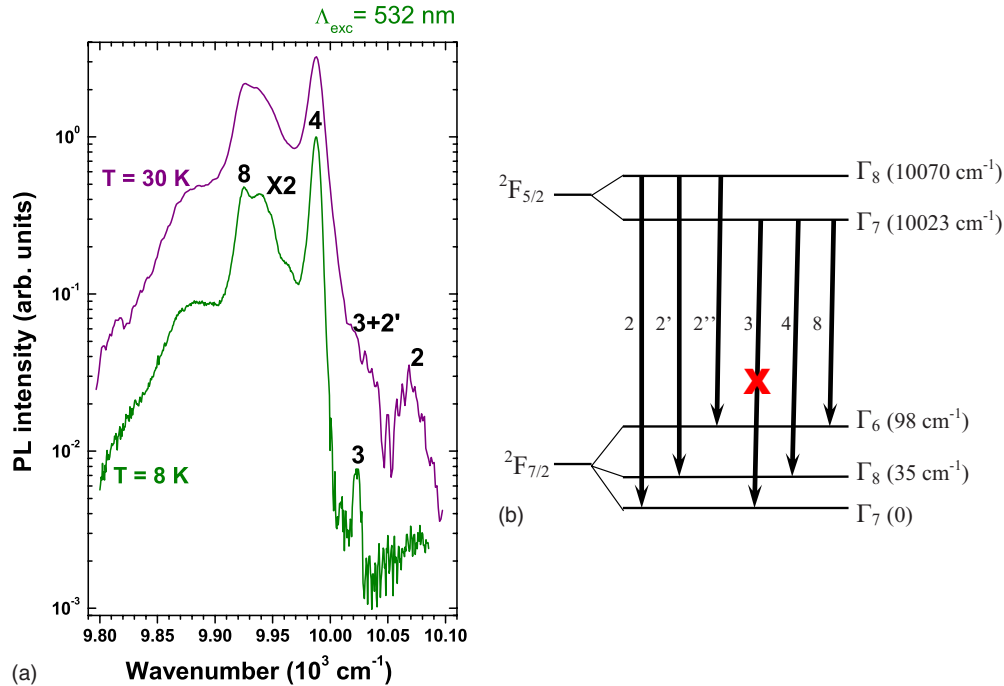


FIG. 1. (Color online) (a) Normalized ambient-pressure PL spectra of InP:Yb excited by the 532 nm laser line at temperatures 8 and 30 K. The spectra are displaced along the vertical axis for clarity. (b) The energy-level diagram of the crystal-field split $4f$ (Ref. 13) levels of Yb^{3+} in InP at ambient pressure with marked electrically dipole allowed and forbidden transitions (crossed). Level assignment: following Ennen *et al.* (Ref. 1). X2 marks the phonon-assisted emission (see Sec. III B in the text).

the pressure of about 10.5 GPa, at which the host crystal undergoes phase transition from zinc blende to rock salt phase) were performed with the use of low-temperature diamond-anvil cell (Diacell Products MCDAC-1). Argon was used as a pressure transmitting medium. The diamond-anvil cell was mounted in an Oxford Optistat CF cryostat equipped with a temperature controller for low-temperature measurements. The samples, cut and polished down to the thickness of 20 μm , were loaded into the cell along with a small ruby crystal. The R_1 -line ruby luminescence was used for pressure calibration.^{27–29} The linewidth of ruby luminescence was also used for monitoring hydrostatic conditions in the DAC. Since we did not notice any important increase in this linewidth with pressure we believe that the hydrostatic conditions were preserved up to the highest pressure applied to the samples.

The low-temperature, high-pressure absorption measurements were performed using a double gasket as the sample chamber. The sample covering the smaller hole into the rear thin gasket was illuminated via an optical fiber coupled to an Ocean Optics DH2000 Deuterium Tungsten Source. The spectra of transmitted light were measured with the use of a GDM-1000 double-grating monochromator in the same configuration as in the case of measuring of the emission spectra.

The decay kinetics of the luminescence have been measured with the use of an SR430 Multichannel Scaler. A large number of decays has been collected in order to obtain a good signal-to-noise ratio. The exciting laser beam has been chopped by an acousto-optic modulator with the transient time below 10 ns. The luminescence decay times were cal-

culated by fitting the decay kinetics with single-exponential dependencies.

III. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

A. Luminescence spectra of bulk InP:Yb crystal at ambient pressure

Figure 1 presents the luminescence spectra of bulk InP:Yb crystal measured at $T=8$ and 30 K in the semilogarithmic scale (a) along with the electronic energy structure of the Yb ion substituting indium in indium phosphide (b). The electronic energy levels ordering has been chosen taking into account the results of previous photoluminescence,^{1,5,6,8} photoluminescence excitation,⁷ and magnetospectroscopic studies.³⁰ The ground $^2F_{7/2}$ state is split into three components (Γ_7 , Γ_8 , and Γ_6) and the excited $^2F_{5/2}$ state—into two (Γ_7 and Γ_8) components. At low temperatures the luminescence originates from the Γ_7 component of the excited state. The PL line at the highest energy (marked as line no. 3 in Fig. 1) (Ref. 31) arises from the electric dipole forbidden $\Gamma_7 \rightarrow \Gamma_7$ transition, therefore its intensity is very low as compared to the other lines. At elevated temperatures a part of luminescence comes also from the higher lying Γ_8 component of the $^2F_{5/2}$ excited state, separated from Γ_7 by about 47 cm^{-1} .⁷ The luminescence from the upper component of the excited state partially overlaps with the emission from the lower one, which complicates interpretation of the luminescence at higher temperatures.

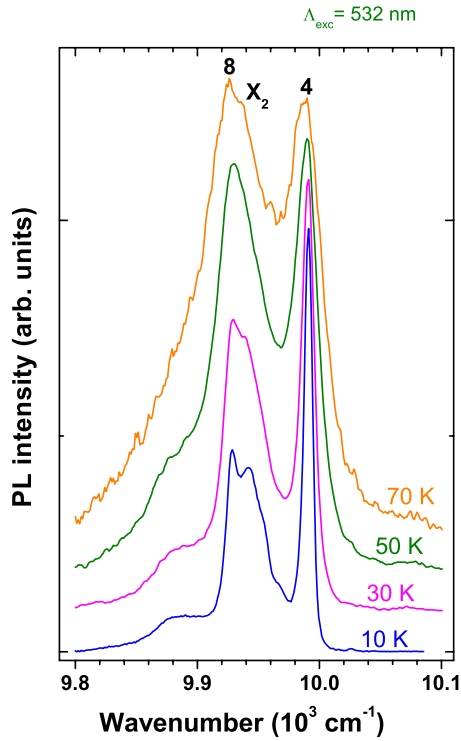


FIG. 2. (Color online) The temperature dependence of the InP:Yb luminescence spectra at ambient pressure, excited by 532 nm laser line. The spectra are normalized to the same intensity of the $\Gamma_7 \rightarrow \Gamma_8$ luminescence line and shifted along the vertical axis for clarity.

B. Temperature dependence of the luminescence

Figure 2 shows the temperature dependence of the InP:Yb luminescence spectra. The spectra are normalized to the same intensity of the $\Gamma_7 \rightarrow \Gamma_8$ luminescence line. In reality, the luminescence intensity of the Yb in InP decreases rapidly with temperature and above 80 K it is practically unmeasurable. Such temperature dependence of the luminescence is associated with Auger-type luminescence quenching.¹⁴ Increase in the relative intensity of the luminescence around 9920 cm^{-1} (around line no. 8) as compared to luminescence close to 9980 cm^{-1} (around line no. 4) at higher temperatures is associated with acoustic-phonon-assisted emission marked in Fig. 1(a) as X2.³² Since optical transitions observed in these lines are associated with emission of phonons, their intensity is proportional to $\eta_B + 1$, where η_B is the Bose-Einstein statistics. This explains the increase in the intensity of the line X2 emission with increasing temperature, in spite of lower energy of this line as compared to line nos. 3 and 4. Due to the overlap of the phonon-assisted emission with that associated with pure electronic transition the interpretation of the luminescence spectra of Yb ion in many hosts remains unresolved. That aspect was also for many years the main obstacle in proper identification of electronic transitions in InP:Yb. In Figs. 2 and 3 the major lines associated with phonon-assisted emission are labeled as X1 and X2.

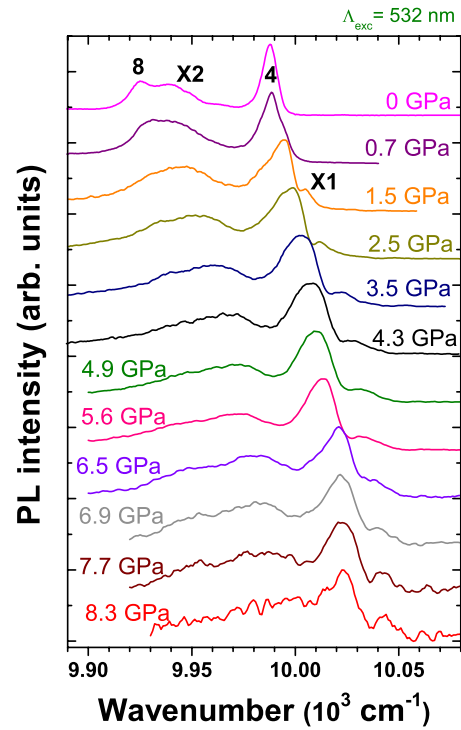


FIG. 3. (Color online) Normalized PL spectra of InP:Yb sample at pressures from 0 to 8.3 GPa measured at $T=10 \text{ K}$.

C. Pressure dependence of luminescence spectra and decay kinetics at low temperature

1. Experimental results

The pressure dependence of the luminescence spectra of Yb in InP is presented in Fig. 3. All luminescence lines exhibit linear shifts toward higher energies as pressure increases with pressure coefficients in the range of $(4-8) \text{ cm}^{-1}/\text{GPa}$ up to about 6 GPa. Above 6 GPa the peak positions of the luminescence lines become almost pressure independent. Positions of the major luminescence lines, both associated with the electronic (line nos. 3, 4, and 8) and with phonon-assisted transitions (X1 and X2) as a function of pressure are shown in Fig. 4. The pressure coefficients of the linear parts of particular lines and their spectral positions at ambient pressure are collected in Table I.

The measured decay times of the luminescence are on the order of $10-15 \mu\text{s}$ and are determined mainly by the non-radiative Auger effects. They exhibit a relatively weak pressure dependencies, what is in good agreement with previous results.¹⁴

2. Theoretical analysis

The Hamiltonian, which describes the energy structure of the Yb^{3+} ion in a crystal field of T_d symmetry can be expressed as³³

$$\mathbf{H} = \mathbf{H}_{\text{SO}} + \mathbf{H}_{\text{CF}}, \quad (1)$$

where \mathbf{H}_{SO} represents spin-orbit (SO) interaction and \mathbf{H}_{CF} is a crystal-field Hamiltonian. We neglect very small second-order interaction between the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets.

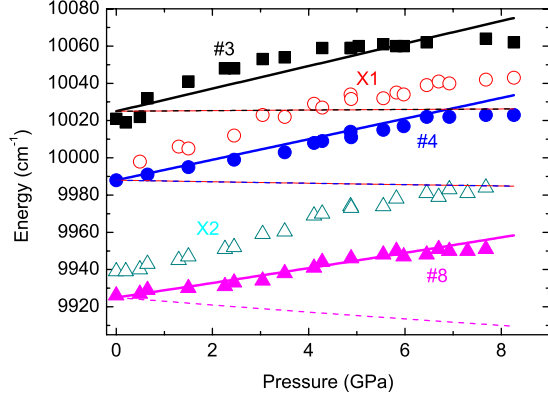


FIG. 4. (Color online) Position of the major luminescence lines of InP:Yb as a function of pressure. Dashed lines: the theoretical dependencies with pressure-independent spin-orbit constant and solid lines: the theoretical dependencies with pressure-dependent spin-orbit constant (see Sec. III C 2).

The spin-orbit interaction is responsible for the splitting of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ states, which is equal to $(7/2)\lambda$, where λ is a spin-orbit parameter. Suitable crystal-field Hamiltonian for a center with cubic symmetry can be expressed in terms of equivalent operators,

$$H_{CF} = B_4 O_4 + B_6 O_6, \quad (2)$$

where $O_4 = O_4^0 + 5O_4^4$ and $O_6 = O_6^0 - 21O_6^4$ represent the fourth and sixth order angular momentum operators, and B_4 and B_6 are corresponding coefficients, which values are determined experimentally.

Application of the crystal-field operators [Eq. (2)] to the ground state with $J=7/2$ and to the excited state with $J=5/2$ yields the following equations³⁰ for the transition energy between the first excited sublevel Γ_7 of the ${}^2F_{5/2}$ state and the ground state ${}^2F_{5/2}$ sublevels with Γ_7 , Γ_8 , and Γ_6 symmetries,

$$\Gamma_7({}^2F_{5/2}) \rightarrow \Gamma_7({}^2F_{7/2}): \quad E(\#3) = -(7/2)\lambda + (10/3)b_4 + 12b_6, \quad (3a)$$

$$\Gamma_7({}^2F_{5/2}) \rightarrow \Gamma_8({}^2F_{7/2}): \quad E(\#4) = -(7/2)\lambda - (50/3)b_4 - 16b_6, \quad (3b)$$

$$\Gamma_7({}^2F_{5/2}) \rightarrow \Gamma_6({}^2F_{7/2}): \quad E(\#8) = -(7/2)\lambda - (86/3)b_4 + 20b_6, \quad (3c)$$

where $\Delta E({}^2F_{5/2}) = 22b_4$ is equal to the energy separation between the Γ_7 and Γ_8 sublevels of the excited ${}^2F_{5/2}$ state. Here $b_i = B_i F(i)$, where $F(4) = 60$ and $F(6) = 1260$.^{33,34} Solving these equations for λ , b_4 , and b_6 and using experimental values of the energies of the appropriate transition lines at ambient pressure one obtains the following values: $\lambda^{amb} = -2864.14 \text{ cm}^{-1}$; $b_6^{amb} = -0.7727 \text{ cm}^{-1}$; and $b_4^{amb} = 2.9318 \text{ cm}^{-1}$.

In accordance with point-charge model the b_4 and b_6 parameters should be dependent on the distance, R , between the central ion and ligands in the following way:³³

$$b_4 \propto R^{-5}; \quad b_6 \propto R^{-7}. \quad (4)$$

For calculation of the pressure dependence of the central ion-ligand distances $R_{pressure}$ we used the following formula, derived from the Murnaghan equation of state:³⁵

$$\frac{R_0}{R_{pressure}} = \left(\frac{pK'_0}{K_0} + 1 \right)^{1/3K'_0}, \quad (5)$$

where R_0 is the In-P distance in indium phosphide at ambient pressure ($R_0 = 2.54 \text{ \AA}$),³⁶ and K_0 and K'_0 are the values of bulk modulus and its pressure derivative ($K_0 = 71.1 \text{ GPa}$ and $K'_0 = 4.59 \text{ GPa}$),³⁷ respectively.

Using Eq. (3) with the pressure dependence of the Yb-P distance described by Eqs. (4) and (5), one can obtain the pressure relationships of the positions of the Yb^{3+} electronic levels in InP. Those dependencies are marked in Fig. 4 as dashed lines. As one can see, they do not describe properly the experimental results. Covalency effects, which may be expected in this system, and different local compressibility around a dopant than observed in the bulk crystal can affect the values of the exponents in Eq. (4). However use of even quite different (much larger or smaller) values of exponents in Eq. (4) does not remove the discrepancy between this model and the experimentally observed dependencies.

A much better agreement can be obtained if one assumes that the spin-orbit interaction, responsible for the splitting between the ground ${}^2F_{7/2}$ and excited ${}^2F_{5/2}$ states, is pressure dependent. The increase in the spin-orbit constant $\lambda_{pressure}$

TABLE I. Spectral positions of the major luminescence lines of Yb^{3+} in InP at ambient pressure and their pressure coefficients associated with the electronic (line nos. 3, 4, and 8) (Ref. 1) and with phonon-assisted transitions (X1 and X2) (Ref. 32).

Line label	Assignment	Line spectral position E (cm ⁻¹)	dE/dp (cm ⁻¹ /GPa)
No. 3	$\Gamma_7 \rightarrow \Gamma_7$	10024 ± 4	7.6 ± 0.7
X1	Vibrational sideband	9996 ± 2	7.2 ± 0.5
No. 4	$\Gamma_7 \rightarrow \Gamma_8$	9987 ± 1	5.0 ± 0.2
X2	Vibrational sideband	9937 ± 1	7.1 ± 0.3
No. 8	$\Gamma_7 \rightarrow \Gamma_6$	9924 ± 1	4.2 ± 0.3

with pressure can be described by a linear dependence, in agreement with linear dependence of Yb^{3+} transition energies, observed up to ~ 6 GPa,

$$\lambda_{\text{pressure}} = \lambda_{\text{amb}} + k \cdot p, \quad (6)$$

where λ_{amb} is a value of spin-orbit coupling at ambient pressure and k is its pressure derivative. The best fit to the experimental dependencies of the energy of the electronic transitions of the Yb^{3+} ion in the range of the linearity (between ambient pressure and ~ 6 GPa) is obtained if $k = 0.0059 \text{ cm}^{-1}/\text{GPa}$. These fits are presented in Fig. 4 as solid lines. The quality of the fits in the region of pressure up to 6 GPa is very good.

The increase in the spin-orbit interaction strength is associated with covalency effects which change the spin-orbit parameter λ of Yb^{3+} ions. This change may be due to the admixture of ligands (phosphorus) electronic functions to the f function of Yb dopant, so the effective function of f electrons is not limited to the volume occupied by the Yb^{3+} ion. This mainly contributes to the variation in λ with the pressure. If the effective SO coupling parameter is averaged over such an extended function then contributions from the atomic SO parameters of the ligands exist. Similar effects have been previously observed in several systems doped with other rare-earth ions^{38–42} as well as in II-VI semiconductors doped with Cr^{2+} .⁴³ The SO parameter increases strongly with atomic number of ions, therefore the covalency effects contribute much more to change the SO parameter of Yb^{3+} in InP as compared with that for Yb^{3+} in GaN, where such effects are negligible.⁴⁴

At the values of pressure above 6 GPa the experimental positions of the luminescence lines become almost pressure independent. Such behavior was observed previously and ascribed to pressure-induced energy structure changes in the cubic Yb^{3+} center.⁴⁵ It was suggested that the effect was associated with the certain crossing of the ytterbium ion energy levels, either in the excited state or in the ground state. Our analysis presented above [see Eq. (3) and the following text] shows that such a situation is excluded.

Thus we would like to propose another explanation of the observed effect. The level crossing occurs between the Yb^{3+} excited $^2F_{5/2}$ state and a charge-transfer level identified in InP:Yb by authors of Ref. 46, who based on the time-resolved photoluminescence studies and established the energy diagram of the Yb ion in InP cubic lattice site with one extra electron. They described two acceptor levels for the Yb^{3+} ion in the band gap of InP at energies equal to $E_{\text{CBM}} - 30 \text{ meV}$ and $E_{\text{VBM}} + 150 \text{ meV}$ [E_{CBM} —energy of conduction-band minimum (CBM) and E_{VBM} —energy of valence-band maximum (VBM)]. Such level crossing is highly probable since pressure coefficients of the band states of InP associated with the charge-transfer process are significantly greater from the pressure coefficients of deep levels of Yb^{3+} ion. The results of the studies of pressure influence on the band gap of InP are presented in Sec. III D.

D. Pressure dependence of absorption spectra at low temperature

The absorption spectra of InP:Yb have been measured in the pressure range from 0 up to 10.6 GPa. Because of small

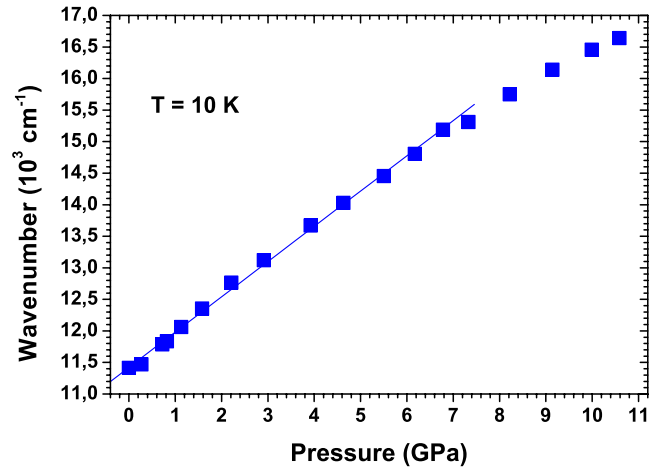


FIG. 5. (Color online) Pressure dependence of the band gap E_g of InP measured at $T = 10$ K. The solid line represents a linear fit to the experimental data.

amount of Yb^{3+} dopant and very low thickness of the sample that can be loaded into the DAC, the ytterbium absorption was not detectable and only the absorption edge of InP crystal host could be observed. The pressure dependence of the band gap E_g measured at liquid-helium temperature is presented in Fig. 5. It shows some deviation from linearity at higher pressure, so according to Prins *et al.*⁴⁷ the pressure coefficient has to be determined by linear fit to the data for the pressure range limited to 7 GPa. So obtained energy gap of InP at ambient pressure equals to $E_g = 11422 \pm 28 \text{ cm}^{-1}$ ($1.416 \pm 0.04 \text{ eV}$) and its pressure coefficient is $559 \pm 8 \text{ cm}^{-1}/\text{GPa}$ ($69 \pm 1 \text{ meV}/\text{GPa}$). These values are in agreement with those obtained from absorption^{18,22} and luminescence measurements,^{19,21} although the results are slightly dependent on the carrier concentration in the examined samples. In order to obtain reliable data we performed absorption measurements under pressure on the same sample as used in all experiments presented here.

The pressure coefficient of the InP band gap is about two orders of magnitude higher than pressure coefficients of Yb^{3+} levels. This leads to an increase in energy interval between the conduction-band minimum of InP host and charge-transfer states of Yb. To investigate the changes in energy interval between ytterbium excited levels and the valence-band maximum of InP host we use the theoretical predictions⁴⁸ and experimental results,⁴⁹ according to which the volume deformation potential of InP VBM is negative, i.e., the energy of the VBM increases with pressure increase. Using the value of the CBM deformation potential determined by deep-level transient spectroscopy of transition-metal defect levels⁴⁹ $a_c = (-7 \pm 1) \text{ eV}$ yields the pressure coefficient of CBM,⁴⁸

$$\frac{dE_{\text{CBM}}}{dp} = -\frac{a_c}{K_0} \quad (7)$$

equal to about 98 meV/GPa. Taking into account our results of pressure dependence of the energy gap, we obtain the pressure coefficient of the VBM as $+29 \text{ meV}/\text{GPa}$. This

yields the 150 meV increase in the VBM energy at the pressure of 5.2 GPa. Assuming that the position of the Yb³⁺ related levels in InP is determined with reference to the vacuum level while neglecting their relatively low-pressure coefficients (<1 meV/GPa), we could expect that approximately at this pressure the VBM energy reaches the acceptor level of Yb described by Bohnert *et al.*⁴⁶ This pressure value agrees quite well with the pressure, at which the Yb³⁺ luminescence lines become almost pressure independent.

Another possible explanation of the observed effect can be associated with certain peculiarities of the covalency effects, which could modulate the values of the spin-orbit parameter λ in such a way that it becomes pressure independent above 6 GPa, in spite of the pronounced dependency at lower pressure. This issue requires further experimental and theoretical studies, which are going to be performed.

IV. SUMMARY AND CONCLUSIONS

We have studied the influence of high hydrostatic pressure on the luminescence spectra and radiative decay times of the intrashell f - f transitions of Yb³⁺ ions in bulk InP crystals and on band-gap absorption of indium phosphide with the use of diamond-anvil cell technique at low temperatures.

It is shown that the energies of intrashell f - f transitions ($^2F_{5/2} \rightarrow ^2F_{7/2}$) of Yb³⁺ ions in InP crystals are sensitive to the applied hydrostatic pressure and exhibit an appreciable

increase up to about 6 GPa. This effect is determined by the increase in the effective spin-orbit parameter of Yb³⁺ ions due to the covalency effects, i.e., the mixing of the Yb wave functions with those of the surrounding P³⁻ ions. Fitting of the observed pressure dependence of the luminescence transitions yields a value of the pressure coefficient of the spin-orbit parameter of Yb³⁺ ions in InP as 0.0059 cm⁻¹/GPa. At higher pressures the energies of the Yb³⁺ intrashell transitions became almost pressure independent. A tentative explanation is provided in terms of an effect of interaction of Yb³⁺ excited level with the maximum of the valence band which approaches the Yb³⁺ excited state at pressure of about 6 GPa.

At present, the effect of pressure dependence of the spin-orbit interaction due to the increased covalency is theoretically not well described in the literature. Further work is necessary to explain this effect.

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- ¹H. Ennen, U. Kaufmann, G. Pomrenke, J. Schneider, J. Windscheif, and A. Axmann, *J. Cryst. Growth* **64**, 165 (1983).
²H. J. Lozykowski, W. M. Jadwisieniczak, J. Han, and I. G. Brown, *Appl. Phys. Lett.* **77**, 767 (2000).
³T. Andreev, Y. Hori, X. Biquard, E. Monroy, D. Jalabert, A. Farchi, M. Tanaka, O. Oda, L. S. Dang, and B. Daudin, *Superlattices Microstruct.* **36**, 707 (2004).
⁴S. W. Choi, S. Emura, S. Kimura, M. S. Kim, Y. K. Zhou, N. Teraguchi, A. Suzuki, A. Yanase, and H. Asahi, *J. Alloys Compd.* **408-412**, 717 (2006).
⁵V. A. Kasatkin, V. F. Masterov, V. V. Romanov, B. E. Samorukov, and K. F. Shtelmakh, *Fiz. Tekh. Poluprovodn.* **16**, 173 (1982) [*Sov. Phys. Semicond.* **16**, 106 (1982)].
⁶V. F. Masterov, V. V. Romanov, and K. F. Shtelmakh, *Fiz. Tverd. Tela (Leningrad)* **25**, 1435 (1983) [*Sov. Phys. Solid State* **25**, 824 (1983)].
⁷J. Wagner, J. Windscheif, and H. Ennen, *Phys. Rev. B* **30**, 6230 (1984).
⁸G. Aszodi, J. Weber, Ch. Uihlein, L. Pu-lin, H. Ennen, U. Kaufmann, J. Schneider, and J. Windscheif, *Phys. Rev. B* **31**, 7767 (1985).
⁹W. H. Haydl, H. D. Müller, H. Ennen, W. Körber, and K. W. Benz, *Appl. Phys. Lett.* **46**, 870 (1985).
¹⁰J. A. DeLuca and F. S. Ham, *J. Electrochem. Soc.* **124**, 1592 (1977).
¹¹A. Brenier and G. Boulon, *Europhys. Lett.* **55**, 647 (2001).
¹²M. Ramirez, L. Bausa, S. W. Biernacki, A. Kamińska, A. Suchocki, and M. Grinberg, *Phys. Rev. B* **72**, 224104 (2005).
¹³A. Kamińska, S. Biernacki, S. Kobayakov, A. Suchocki, G. Boulon, M. O. Ramirez, and L. Bausa, *Phys. Rev. B* **75**, 174111 (2007).
¹⁴W. Körber and A. Hangleiter, *Appl. Phys. Lett.* **52**, 114 (1988).
¹⁵W. Körber, J. Weber, A. Hangleiter, K. W. Benz, H. Ennen, and H. D. Müller, *J. Cryst. Growth* **79**, 741 (1986).
¹⁶L. A. Hemstreet, in *Materials Science Forum*, edited by H. J. von Bardeleben (Trans Tech, Aedermannsdorf, Switzerland, 1986), Vol. 10-12, pp. 85–90.
¹⁷J. P. Rino and P. S. Branício, *Phys. Status Solidi B* **244**, 239 (2007) b.
¹⁸M. F. Whitaker, S. J. Webb, and D. J. Dunstan, *J. Phys.: Condens. Matter* **10**, 8611 (1998).
¹⁹M. Leroux, *Semicond. Sci. Technol.* **4**, 231 (1989).
²⁰C. S. Menoni and I. L. Spain, *Phys. Rev. B* **35**, 7520 (1987).
²¹C. S. Menoni, H. D. Hochheimer, and I. L. Spain, *Phys. Rev. B* **33**, 5896 (1986).
²²H. Müller, R. Trommer, M. Cardona, and P. Vogl, *Phys. Rev. B* **21**, 4879 (1980).
²³T. Kobayashi, K. Aoki, K. Yamamoto, *Physica B* **139-140**, 537 (1986).
²⁴N. Bouarissa, *Solid-State Electron.* **44**, 2193 (2000).
²⁵I. Gorczyca, N. E. Christensen, and M. Alouani, *Phys. Rev. B* **39**, 7705 (1989).
²⁶M. Godlewski, A. Kozanecki, J. P. Bergman, and B. Monemar, *Appl. Phys. Lett.* **66**, 493 (1995).
²⁷G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).

- ²⁸H. K. Mao and P. M. Bell, *Science* **200**, 1145 (1978).
- ²⁹W. B. Holzapfel, *J. Appl. Phys.* **93**, 1813 (2003).
- ³⁰I. Gersdorf, Ph.D. thesis, University of Amsterdam, 2001.
- ³¹Numbering of the luminescence lines associated with the electronic transitions follows that in Ref. 1.
- ³²L. K. Ermakov, V. A. Kasatkin, and L. P. Pasechnik, *Opt. Spektrosk.* **57**, 11 (1984) [*Opt. Spectrosc.* **57**, 6 (1984)].
- ³³A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1970), p. 670.
- ³⁴C. Rudowicz and C. Y. Chung, *J. Phys.: Condens. Matter* **16**, 5825 (2004).
- ³⁵F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1944).
- ³⁶C. S. Schnohr, P. Kluth, L. L. Araujo, D. J. Sprouster, A. P. Byrne, G. J. Foran, and M. C. Ridgway, *Phys. Rev. B* **79**, 195203 (2009).
- ³⁷D. N. Nichols, D. S. Rimai, and R. J. Sladek, *Solid State Commun.* **36**, 667 (1980).
- ³⁸T. Gregorian, H. d'Amour-Sturm, and W. B. Holzapfel, *Phys. Rev. B* **39**, 12497 (1989).
- ³⁹Th. Tröster, T. Gregorian, and W. B. Holzapfel, *Phys. Rev. B* **48**, 2960 (1993).
- ⁴⁰C. Bungenstock, Th. Tröster, and W. B. Holzapfel, *Phys. Rev. B* **62**, 7945 (2000).
- ⁴¹F. J. Manjón, S. Jandl, K. Syassen, and J. Y. Gesland, *Phys. Rev. B* **64**, 235108 (2001).
- ⁴²F. J. Manjón, S. Jandl, G. Riou, B. Ferrand, and K. Syassen, *Phys. Rev. B* **69**, 165121 (2004).
- ⁴³S. Trushkin, S. W. Biernacki, L. Van Khoi, A. Kaminska, and A. Suchocki, *New J. Phys.* **10**, 013023 (2008).
- ⁴⁴A. Kaminska, A. Kozanecki, E. Alves, M. Boćkowski, and A. Suchocki (unpublished).
- ⁴⁵A. Stapor, A. Kozanecki, K. Reimann, K. Syassen, J. Weber, M. Moser, and F. Scholz, *Acta Phys. Pol. A* **79**, 315 (1991).
- ⁴⁶G. Bohnert, J. Weber, F. Scholz, and A. Hangleiter, *Appl. Phys. Lett.* **63**, 382 (1993).
- ⁴⁷A. D. Prins, J. L. Sly, and D. J. Dunstan, *Phys. Status Solidi B* **198**, 57 (1996).
- ⁴⁸S.-H. Wei and A. Zunger, *Phys. Rev. B* **60**, 5404 (1999).
- ⁴⁹D. D. Nolte, W. Walukiewicz, and E. E. Haller, *Phys. Rev. Lett.* **59**, 501 (1987).