

Radiative recombination in InSe layered crystal

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For layered *InSe* crystals photoluminescence (PL) spectra are investigated and the corresponding radiative transitions are analyzed. It is found that along with the band-to-band transitions the radiative ones with a participation of impurity levels plays substantial role in the light emission spectrum of the semiconductor. This fact is confirmed by the intensities of the radiative bands for the impurity level – $\alpha(\nu)$ -band transitions and the donor-acceptor recombination. The temperature dependences of the spectrum in the range of 100-300 K had also enabled to establish the dynamics for possibility of these radiative transitions. At temperatures 180-300 K the bands associated with the indirect transitions with participation of indirect free excitons are more intensive. At 100-180 K the intensity of the bands corresponding to the direct transitions with participation of direct free excitons increases. We have determined the energies of the observed PL bands and a band diagram of the corresponding radiative transitions in *InSe* is established.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: InSe, Layered crystal, Photoluminescence, Energy diagram

1. Introduction

InSe crystals are interesting objects for optical investigations including PL measurements. The crystal layered structure favours to this study allowing easily to prepare samples of arbitrary thickness by cleaving them from an ingot. Their mirror like surfaces are practically ideal with a normal parallel to the crystallographic *C* axis. A variety of electronic transitions determines a complicated structure of PL spectra due the presence in the *InSe* energy gap of energy levels of different nature [1-8]. So, *InSe* is an indirect semiconductor [9]. The presence of large concentration of native donors and acceptors, which follows from compensative character of its electric properties [10], results in the existence of corresponding levels. The strong electron-hole interaction in the crystal assists to the appearance of additional levels. It causes the creation of both free and bound excitons.

An analysis of the PL spectra of *InSe* layered crystals shows that different authors have found different PL spectra structure and propose various interpretations for them. It is necessary to specify that *InSe* can be grown from both stoichiometric and nonstoichiometric composition of melts [11]. It also can affect quality of the samples and the structure of PL spectra. Some authors observed the dependence of luminescence intensity on method of samples preparation [3]. In a majority of the papers PL spectra were investigated at temperatures 4.2-77 K due to their weak intensity at higher temperatures.

However, we have observed the intensive PL spectra of *InSe* even at room temperature. Therefore the task of this work was to identify radiative transitions and to study their temperature dynamics.

2. Experimental

Indium monoselenide single crystals were grown by the Bridgman method from a non-stoichiometric melt of the components. This method allows growing crystals of high degree of perfection. They were obtained as ingots of 5-6 cm long and 12-14 mm in diameter. The ingots were cut on disks of 4-5 mm in height from which plane-parallel samples were cleaved. 200-300 μm plates for our measurements were chosen in such a way to avoid their possible deformations and surface scratches.

The PL spectra were measured by using a MDR-3 diffraction monochromator. Its resolution was established in such a way to have the best correlation between PL signal intensity and resolution value. Light-emitting *GaP*-diodes were used as a source of continuous excitation with a radiation wave-length of 0.55 μm . The temperature measurements of the PL spectra were carried out in the range 100-300 K in a cryostat with an accuracy of temperature stabilization of ± 0.1 K. The spectra measurements were carried out in a step of 30 K. The PL spectra were registered by means of a calibrated *Si* photodiode. All the spectra were corrected with respect to the spectral sensitivity of the photodiode. The area of the light spot on the sample surface was of about 0.5 mm^2 .

3. Results of and discussion

A typical PL spectrum of *InSe* at different temperatures is presented in Fig. 1. It consists of many bands of different intensity. At room temperature these bands are marked by letters A, B, C, D, E₁, and E. At some temperatures the spectra are not shown due negligible changes in intensities of the radiation bands and their insignificant energy shift with lowering temperature. The bands A, B, and C are caused by the radiative transitions

with participation of donor and acceptor levels, because these bands are located at the long-wavelength spectral edge. The energy positions of these bands maxima and their intensities do not have pronounced temperature dependence (Fig. 2), that also resides in these levels. The electron transitions from the donor level E_D to the valence band correspond to the most intensive band (C) of three observed bands (Fig. 3). The transitions from the conduction band to the acceptor level E_A correspond to the band B (Fig. 3). Such the identification of the bands is caused by the fact that compensated InSe has electronic conductivity. A partial compensation of the donor levels indicates on less concentration of the acceptor levels and, therefore, the transitions with participation of the acceptor levels E_A have less intensity (the B band) in comparison to the C band. The transitions from the donor to acceptor levels correspond to the weakest band A.

The band D, the most intensive at $T=295$ K from all the bands, corresponds to the indirect band-to-band transitions. Such transitions take place with participation of phonons. According to [12], the D band intensity can be described by equation

$$I(h\nu) \approx \nu^2 (h\nu - E_g^i)^2 \exp\left[-\frac{(h\nu - E_g^i)}{kT}\right], \quad (1)$$

where ν is the frequency of light, h is the Planck constant, E_g^i is the indirect bandgap of InSe, k is the Boltzmann constant, T is absolute temperature. The band calculated according to relation (1) is shown in Fig. 1f by open circles. As one can see, there is good agreement between the theoretical and experimental curves. From comparison of these curves we have established that the value of E_g^i at 100 K is equal to 1.27 eV. Taking into account the D band temperature shift (Fig. 2, $\partial E_g^i/\partial T = -8.5 \times 10^{-5}$ eV/K) it was determined that $E_g^i(295 \text{ K}) = 1.253$ eV. The radiative spectra, attributed to the transitions with participation of the donors E_D and acceptor E_A levels, are determined by an equation analogous to equation (1) but with the energy shift by the energy depth of these levels from the corresponding bands. Thus in order to determine E_D and E_A values it is enough to determine the energy distances between the C-D and B-D maxima. The average values of E_D and E_A measured for several samples are 0.026 and 0.060 eV, respectively. According to [13], the photon energy of the radiative donor-acceptor recombination (the A band) is described by the expression

$$h\nu = E_g^i - (E_A + E_D) + \frac{e^2}{\varepsilon \cdot r}, \quad (2)$$

where e is the electron's charge, ε is the dielectric constant of InSe, r is the distance between the donors and acceptor centers. Take into account that $h\nu(A) = 1.206$ eV and $\varepsilon = 7.36$ [14], we have determined $r = 62.3$ nm.

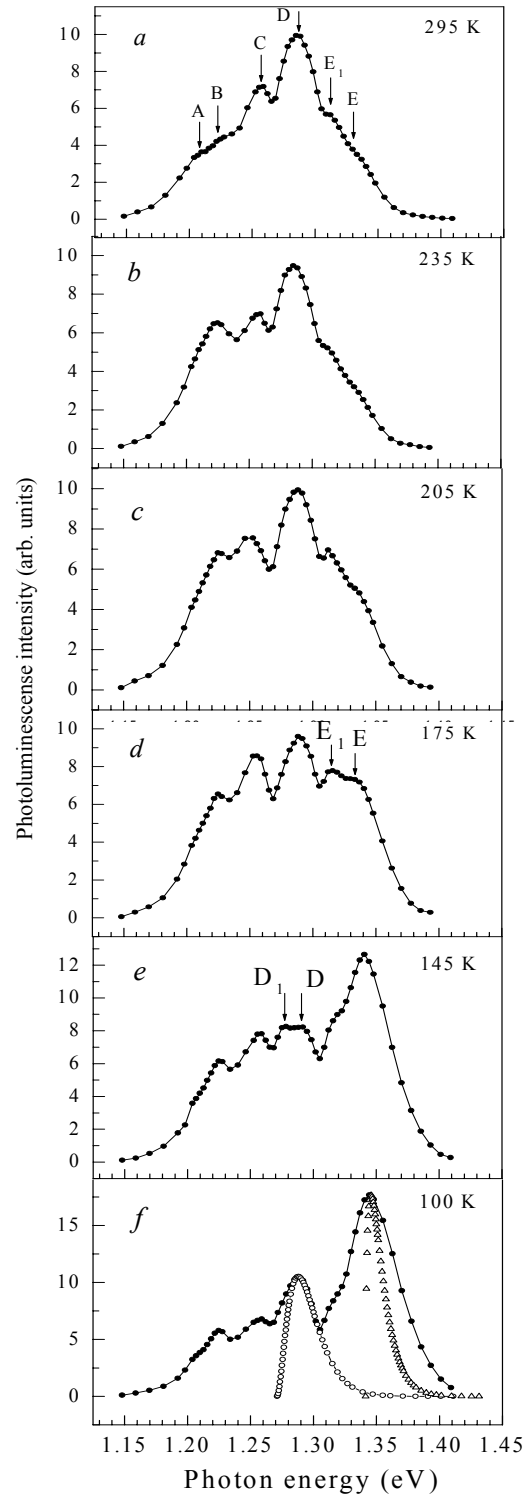


Fig. 1. Photoluminescence spectra of *n*-InSe sample at different temperatures.

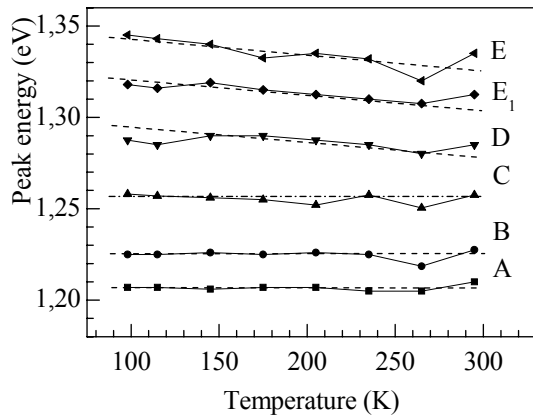


Fig. 2. Temperature shifts of A, B, C, D, E₁ and E peaks.

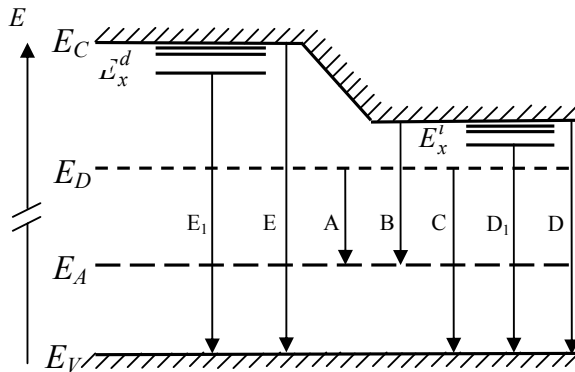


Fig. 3. Energy level diagram of radiative transitions in InSe.

The short-wave length bands E₁ and E correspond to the direct band-to-band transitions. Their intensity sharply increases with lowering temperature whereas that of the D band decreases. In the case of the direct transitions the spectrum of intrinsic radiation has a form [12]:

$$I(h\nu) \approx \nu^2 (h\nu - E_g^d)^{1/2} \exp\left[-\frac{(h\nu - E_g^d)}{kT}\right], \quad (3)$$

where E_g^d is the direct bandgap. The calculated curve is also shown in Fig. 1f. As one can see, the experimental curve is much broader in comparison to the calculated one. $E_g^d(100\text{ K})=1.341$, $E_g^d(295\text{ K})=1.324$ eV. Thus the difference between the E_g^d and E_g^i values is 71 meV.

The temperature dependences of the bands make it possible to establish peculiarities of the D and E bands. Their doublet character is the most well-expressed at 145 K (Fig. 1e) and 175 K (Fig. 1d). The appearance of the D₁ and E₁ bands is caused by the electronic transitions with participation the indirect and direct free excitons from the main excitonic state $n=1$ to the valence band (Fig. 3).

Although it is known from the literature about the direct free exciton binding energy $E_X^d=14.5$ meV [15], there are no data for the indirect ones E_X^i . As one can see from the inserts d and e in Fig. 1, $E_X^d > E_X^i$. Their values are as follows: $E_X^d = 16.9$ and $E_X^i = 13.0$ meV. Note for comparison that thermal energy kT is equal to 15 and 12.5 meV at 175 and 145 K, respectively. It is less than the binding energy of free excitons at these temperatures and, therefore, allowed to observe the doublet character of the D and E bands. At other temperatures this peculiarity disappears due to changes of the intensity of the corresponding transitions.

Note that the excitons bound on impurities determine radiative spectra at helium temperatures. Usually they have weak intensity and, therefore, were not taken into account for interpretation of the obtained spectra.

4. Conclusions

PL spectra of undoped InSe were measured in the temperature range 100 to 295 K. By using comparison of the calculated and experimental spectra we have carried out an analysis of the radiation bands. It made possible to determine parameters of energy levels in InSe. We have established that at T=295 K the direct and indirect energy gaps are $E_g^d=1.324$ and $E_g^i=1.270$ eV, respectively. The temperature shift of the bands is -8.5×10^{-5} eV/K. The binding energies of the free direct and indirect excitons are $E_X^d = 16.9$ and $E_X^i = 13.0$ meV. The energy depths of the donor level below the conduction band bottom and acceptor level above the valence band top are $E_D = 26$ and $E_A = 60$ meV, respectively. Distance between the donor and acceptor centers is equal to 62.3 nm.

References

- [1] A. V. R. Abha, Warriar, J. Appl. Phys. **53**, 5169 (1982).
- [2] Yu. P. Gnatenko, P. A. Skubenko, Yu. I. Zhirko, O. V. Fialkovskaya, Journal of Luminescence, **31 & 32**, 472 (1984).
- [3] T. Ikari, S. Shigetomi, Phys. stat. sol. (b), **124**, K49 (1984).
- [4] J. L. Brebner, T. Steiner, M. L. W. Thewalt, Solid State Communications, **56**, 929 (1985).
- [5] J. Riera, A. Segura, A. Chevy, Phys. stat. sol. (a), **142**, 265 (1994).
- [6] B. Abay, H. Efeoğlu, Y. K. Yoğurtçu, Mat. Res. Bull. **33**, 1401 (1998).
- [7] F. J. Manjón, Y. van de Vijver, A. Segura, V. Muñoz, Z. X. Liu, C. Ulrich, Phys. stat. sol. (b), **211**, 105 (1999).
- [8] A. A. Homs, B. Mari, J. Appl. Phys., **88**, 4654 (2000).

- [9] G. Saintogne, J. L. Brebner, Phys. Review **B30**, 1957 (1984).
- [10] J. Martinez-Pastor, A. Segura, J. L. Valdes, A. Chevy, J. Appl. Phys. **62**, 1477 (1987).
- [11] A. Chevy, A. Kuhn, M.S. Martin, J. Cryst. Growth **38**, 118 (1977).
- [12] C. M. Sze, Physics of semiconductor devices, John Wiley and Sons, New York (1969), in Russian.
- [13] A. A. Bergh, P. J. Dean, Light-emitting diodes, Clarendon Press, Oxford (1976), in Russian.
- [14] Landolt-Börnstein. Numerical Data and Functional Relationships in Science and Technology, New Ser. Group III: Crystal and Solid State Physics, V. 17, sv.f, Ed. by O. Madelung, Berlin e.a., Springer (1983).
- [15] J. Camassel, P. Merle, H. Mathieu, A. Chevy, Phys. Rev. B, **17**, 4718 (1978).

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