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Gain Spectrum for the In_4Se_3 Crystal with a Non-Standard Dispersion Law of Charge Carriers

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Based upon the *ab initio* band structure calculations results and the density of states function of the orthorhombic In_4Se_3 crystal as well as the experimental data concerning its radiative recombination, it was shown that the Bernard–Durafour condition is fulfilled for this crystal. The absorption coefficient α that exhibits a negative value in the given energy range and for the given concentrations of non-equilibrium charge carriers, was calculated.

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1. Crystalline structure and energy spectrum of the In_4Se_3 crystal

Recently, a growing interest to some layered indium selenides [1–3] has occurred due to their non-standard dispersion laws for charge carriers and the possibility to create InSe–In_4Se_3 heterostructures [4]. The layered In_4Se_3 semiconductor belongs to the orthorhombic system and its symmetry is described by the D_{2h}^{12} ($Pnnm$) space group. It is a direct-band-gap material with the smallest energy gap in the Γ point of the Brillouin zone (BZ). The dispersion laws for electrons and holes exhibit a low-energy non-parabolicity due to the presence of the four-power terms of the wave vector $\boldsymbol{k}$. A consequence of this fact is a peak-like density of states function [5]. These peculiarities were observed for the first time in calculations of the band structure of In_4Se_3 crystal by the semi-empirical pseudopotential method [6], confirmed both by the *ab initio* band structure calculations [1] in the framework of density functional theory (DFT), and experimentally [2, 3]. Such a placement of the band extrema favors the radiative recombination of charge carriers, which is the subject of theoretical investigation of this paper. The experimental investigation on the radiative recombination of In_4Se_3 were reported in [7]. In this case, a generation of charge carriers took place by means of the electron beam of the density $j \in (0.2–5.0)$ A/cm^2, with the energy of a single electron $W \in (65–70) \times 10^3$ eV at $T = 90$ K, in the spontaneous and stimulated regimes. These experimental investigations were performed before the band structure of In_4Se_3 has been investigated.

2. Generation and recombination of charge carriers in the In_4Se_3 crystal

The theory of emission and absorption of a two-level system can be applied to a semiconductor [8], when assumed that the number of transitions per time unit from the ground state 1, being a chosen energy level in the valence band, to an excited state 2 in the conduction band, can be given as: $\nu_{12}^{\mathrm{abs}} = B_{12} f_1 (1 - f_2) g_1(E_1) g_2(E_2) Z(E_{12})$, where B_{12} is the Einstein coefficient [9] describing a transition probability, f_1, f_2 are the Fermi–Dirac distribution functions, g_1, g_2 are the density of states functions for the considered levels in the valence and conduction bands, $Z(E_{12})$ is the density of photons. The number of transitions per time unit connected with a stimulated and spontaneous radiation can be described as: $\nu_{21}^{\mathrm{stim}} = B_{21} f_2 (1 - f_1) g_1(E_1) g_2(E_2) Z(E_{12})$, $\nu_{2,1}^{\mathrm{spon}} = A_{21} f_2 (1 - f_1) g_1(E_1) g_2(E_2)$, respectively. In the thermodynamic equilibrium: $\nu_{12}^{\mathrm{abs}} = \nu_{21}^{\mathrm{stim}} + \nu_{21}^{\mathrm{spon}}$ and the following relation between the density of photons and the Einstein coefficients results from this relation: $Z(E_{12}) = A_{21}/[B_{12} \exp((E_2 - E_1)/k_{\mathrm{B}}T) - B_{21}]$. The density of photons $Z(E_{12}) = Z(E_{21}) = Z(E)$ can be obtained independently of the Planck theory [8]:

$$Z(E) = \frac{8\pi n^3 E_{12}^2 \left(1 + \frac{E_{21}}{n} \frac{\mathrm{d}n}{\mathrm{d}E}\right)}{c^3 h^3 [\exp(E_{21}/k_{\mathrm{B}}T) - 1]}, \tag{1}$$

where n is a refraction coefficient.

The following relation between the Einstein coefficients A_{21}, B_{12}, B_{21} is obtained from the last two equations: $A_{21} = 8\pi n^3 E_{21}^2 B_{21}/c^3 h^3$, $B_{12} = B_{21}$. A condition necessary for the stimulated emission process to occur in the considered system is obtained by assuming that $\nu_{21}^{\mathrm{stim}} > \nu_{12}^{\mathrm{abs}}$, which implies the Bernard–Durafour condition: $E_2 - E_1 < E_{f_2} - E_{f_1}$ [10], where E_{f_2} and E_{f_1} are the quasi-Fermi levels of the non-equilibrium carriers present in the conduction and valence bands, respectively. When the absorption processes (transitions 1–2) prevail over the emission ones (transitions 2–1), then the absorption coefficient α is positive, else it is negative and is connected with the population inversion, for which

$\alpha(E_{21}) = B_{12}(f_1 - f_2)n/c$ [8]. The Einstein coefficient B_{12} can be obtained by applying the time-dependent perturbation theory to describe an interaction between electrons in the solid state with the electromagnetic radiation.

Let $\psi_1(\boldsymbol{r},t)$, $\psi_2(\boldsymbol{r},t)$ be the wave functions describing the initial and final stationary state, and the perturbation operator $\hat{H}^{(\mathrm{int})} = -e/m\boldsymbol{A}\cdot\hat{p}$, where $\boldsymbol{A}$ is a vector potential of the electromagnetic field. Taking into account that $\boldsymbol{E} = -\partial\boldsymbol{A}/\partial t$, where $\boldsymbol{E}$ is the strength of the electromagnetic field, one obtains $\boldsymbol{E} = \boldsymbol{E}_0\exp(\mathrm{i}(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})) + \boldsymbol{E}_0^*\exp(-\mathrm{i}(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})) = 2E_0\boldsymbol{n}\cos(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})$, and hence $\boldsymbol{A} = -2(2\hbar/\varepsilon_0 n^2\omega)^{\frac{1}{2}}\boldsymbol{n}\sin(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})$, since $E_0^2 = 2\hbar\omega/\varepsilon_0 n^2$ [8]. Then

$$B_{12} = \frac{1}{t}\left|\frac{1}{\mathrm{i}\hbar}\int_0^t \langle\psi_1|\hat{H}^{(\mathrm{int})}(t')|\psi_2\rangle\,\mathrm{e}^{\mathrm{i}\,\omega_{12}t'}\,\mathrm{d}t'\right|^2$$

$$= \frac{2\pi}{\hbar}\frac{2e^2\hbar^2}{m^2\varepsilon_0 n^2\hbar\omega}\left|\langle\psi_1|\hat{p}|\psi_2\rangle\right|^2\delta(E_2 - E_1 - \hbar\omega) \quad (2)$$

$$= \frac{A}{\hbar\omega}|M_{12}|^2\delta(E_2 - E_1 - \hbar\omega)\,, \quad (3)$$

where A is a constant. Unlike in the case of a two-level system, for a semiconductor, there exists continuum of states in the valence and conduction band that are described by the density of states functions $g_{\mathrm{v}}(E_{\mathrm{v}} - E_1)$ and $g_{\mathrm{c}}(E_2 - E_{\mathrm{c}})$. Therefore, the absorption coefficient α with energy $\hbar\omega$ should be equal to the sum of absorption coefficients $\hbar\omega$ of photons for all pairs of levels placed on this energetic distance. This sum can be written as the integral

$$\alpha(\hbar\omega) \sim \frac{1}{\hbar\omega}\int_{-\infty}^{+\infty}|M_{12}|^2 n/c[(f_{\mathrm{v}}(E_1) - f_{\mathrm{c}}(E_2))]$$

$$\times\, g_{\mathrm{v}}(E_{\mathrm{v}} - E_1)g_{\mathrm{c}}(E_2 - E_{\mathrm{c}})\delta(E_2 - E_1 - \hbar\omega)\,\mathrm{d}E_1\,. \quad (4)$$

Here obviously $E_2 - E_1 = \hbar\omega$. An analytic form of the density of states function $g(E)$ for the In_4Se_3 crystal is known neither for the conduction band bottom, nor for the top of the valence band. Therefore, to calculate the coefficient α for In_4Se_3 from Eq. (4) we switch to the variables k_x, k_y, k_z of the wave vector

$$\alpha(\hbar\omega) = \frac{A}{\hbar\omega}\int_{\mathrm{BZ}}|M_{12}|^2 n/c\{f_{\mathrm{v}}[E_{\mathrm{v}}(\boldsymbol{k})] - f_{\mathrm{c}}[E_{\mathrm{c}}(\boldsymbol{k})]\}$$

$$\times\,\delta(E_{\mathrm{c}}(\boldsymbol{k}) - E_{\mathrm{v}}(\boldsymbol{k}) - \hbar\omega)\,\mathrm{d}^3\boldsymbol{k}\,. \quad (5)$$

As can be seen from (5), to calculate α, one should find a value of the matrix element M for all those k-points which describe the top of the valence and the bottom of the conduction bands, and for which the energetic distance corresponds to the photon energy $\hbar\omega$. To calculate the matrix element M we used the wave functions in the form of a combination of the plane waves, following from the *ab initio* band structure calculations of the In_4Se_3 crystal [1].

3. Results and discussion

The quasi-Fermi levels $E_{f\mathrm{v}}(\boldsymbol{k})$ and $E_{f\mathrm{c}}(\boldsymbol{k})$ depend on the concentration of the non-equilibrium charge carriers. Therefore, we calculated dependence of these levels on concentration, that is presented in Fig. 1. We estimated the non-equilibrium concentration of electrons and holes in In_4Se_3 based upon experimental data [7], by calculating firstly the energy E_0, necessary to create one electron–hole pair: $E_0 \approx 3E_{\mathrm{g}}$ [11] for the average value of the experimental band gap $E_{\mathrm{g}} = 0.7$ eV, known from the kinetic investigations [12], and next, the multiplicity coefficient $\nu_{\mathrm{e}} = W/E_0 = 3.4\times10^4$ electron–hole pairs (for $W = 68\times10^3$ eV). Finally, the concentration of the non-equilibrium electrons $\Delta n = j\tau\nu_{\mathrm{e}}/ed$ belongs to the range 10^{19}–10^{20} cm^{-3} (for $j = 5.0$ A/cm^2). We assumed in calculations that the radiative lifetime τ of an electron–hole pair is in the range 10^{-6}–10^{-7} s, that is characteristic for typical semiconductors [13], and the penetration depth of electrons from the beam $d \approx 10^{-6}$ cm, that correspond to the energy $W \approx 10^4$–10^5 eV [14]. The obtained value $\Delta n = \Delta p$ allows to estimate the energetic positions of the quasi-Fermi levels for electrons and holes. The calculated energy distance $E_{f\mathrm{c}} - E_{f\mathrm{v}} = 0.94$ eV (for $n \sim \Delta n = 10^{19}$ cm^{-3}) which ensures that the Bernard–Durafour criterion is fulfilled.

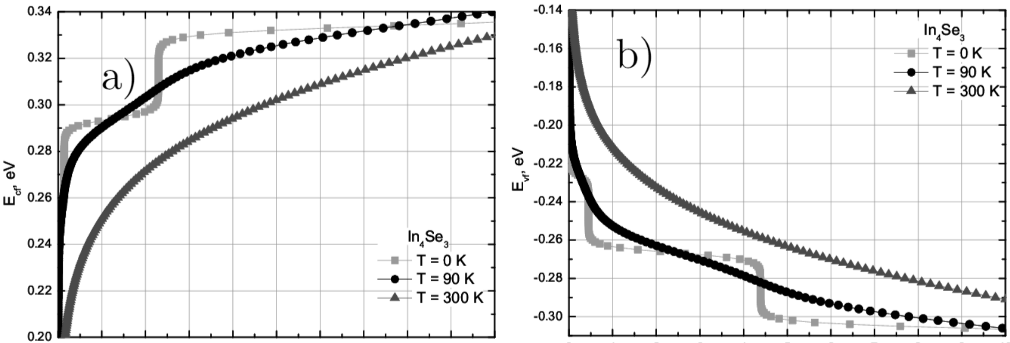

Fig. 1. Dependence of the quasi-Fermi levels of non-equilibrium electrons (a) and holes (b) vs. their concentration in In_4Se_3.

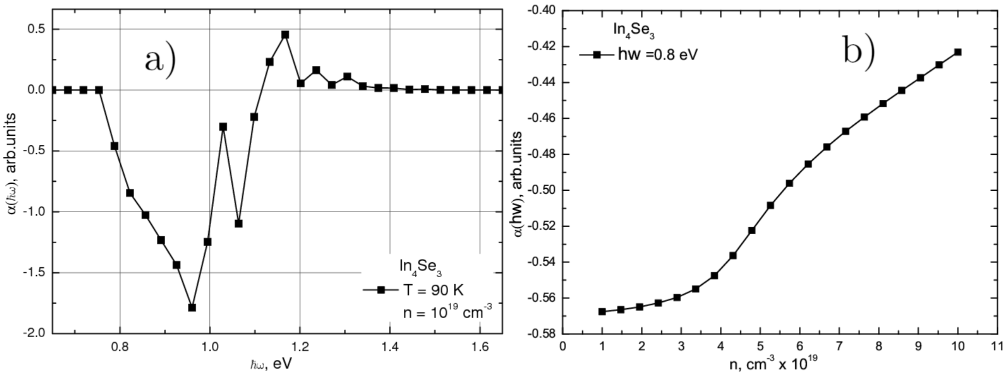

Fig. 2. (a) Absorption coefficient vs. photon energy, (b) dependence of the absorption coefficient on the non-equilibrium concentration of carriers for In_4Se_3.

Figure 2a shows results of numerical calculations of the α coefficient vs. $\hbar\omega$ at 90 K for which the stimulated radiation measurements were done for In_4Se_3. As can be seen, $\alpha < 0$ in the range (0.75, 1.10) eV which ensures a possibility of the stimulated radiation. Figure 2b displays a dependence of the absorption coefficient on the non-equilibrium concentration of charge carriers at the energy corresponding to the peak of the stimulated radiation. The obtained energy values corresponding to $\alpha < 0$ are in agreement with the experimental data for the In_4Se_3 crystal, which indicates that the chosen values of the penetration depth $d = 10^{-6}$ cm and the lifetime $\tau \approx 10^{-6}$ s are correct for the In_4Se_3 crystal. The peak-like density of states function near the energy gap in In_4Se_3 does not make it difficult to enter the quasi-Fermi levels into the valence and conduction bands. Therefore, the Bernard–Durafour criterion can be fulfilled, and in consequence, the radiative recombination takes place in this crystal.

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