Y.M. STAKHIRA, R.Y. STAKHIRA

Ivan Franko National University of Lviv
(50, Drahomanov Str., Lviv 79005, Ukraine; e-mail: stakhira@electronics.lnu.edu.ua)

MECHANISM OF NON-STATIONARY PIEZOPHOTOCONDUCTIVITY SPECTRUM FORMATION IN LAYERED CRYSTALS

Changes in the structure of electron states in layered crystals caused by a shear deformation of layers under the action of an external low-frequency modulated pressure have been analyzed. It is shown that the strain generates a superstructure with a period in the direction perpendicular to the layers, being a multiple of the layer thickness. The interaction of electrons with the strain-perturbed potential gives rise to the appearance of regularly located gaps in the energy dependence on the wave vector and results in a redistribution of electrons over the band states by means of Umklapp processes. A balance equation for the population of states is proposed, and its dynamics is analyzed. The non-stationary component of the interband absorption coefficient is estimated. The spectrum of this component is shown to have a band-like character, with the harmonic at the modulation frequency being shifted in phase with respect to the pressure phase by an angle depending on the light quantum energy.

K e y w o r d s: layered crystals, Umklapp's processes, piezophotoconductivity, interband absorption.

1. Introduction

The mechanical stress created by an external action in a semiconductor gives rise to certain changes in the structure of electron states. As a result, the stress can manifest itself in specific electron phenomena and properties as a modulating factor. Such phenomena include, in particular, piezophotoconductivity, a component of the semiconductor conductivity emerging owing to the mutual action of light and a mechanical stress on the electron subsystem and proportional to the product of the light intensity and the mechanical stress [1].

Experimental researches of piezophotoconductivity in semiconductors with a layered structure [2–4], when the specimens were subjected to the light irradiation with a constant intensity and a low-frequency deformation, revealed a number of nontrivial properties, which were typical of this combined conductivity. In particular, in the interval of light frequencies where interband transitions were realized, the spectra of a harmonic component with the frequency equal to the modulation one had an oscillatory character, which manifested itself in a regular arrangement—in the whole spectral range—of narrow spectral inter-

vals where an enhanced piezophotoconductivity took place. In addition, the dependence of a piezophotoconductivity phase shift with respect to the phase of a modulating pressure on the light quantum energy was revealed. The magnitude of this shift could reach a value of $\pi/2$. In Fig. 1, the spectra of the piezophotoconductivity of In_4Se_3 crystals and the relative phase shift [2] are shown, which illustrate the typical properties of piezophotoconductivity spectra inherent to layered crystals.

The overall evaluation of the piezophotoconductivity properties and the features in the structure of relevant spectra testifies that they cannot be associated exclusively with the stationary structure of semiconductor bands. It is evident that the crucial role in the formation of those spectra is played by the processes of generation and recombination of nonequilibrium charge carriers, when light and a mechanical stress jointly affect the electron subsystem of a semiconductor. Regarding this mutual action as a factor that gives rise to a combined perturbation of electron states and corresponding interband transitions, we would like to emphasize a substantial role of the mechanical stress in the dynamics of generation and recombination. This work is aimed at evaluating the possible changes in the structure of semiconductor electron states induced by deformation and, on this
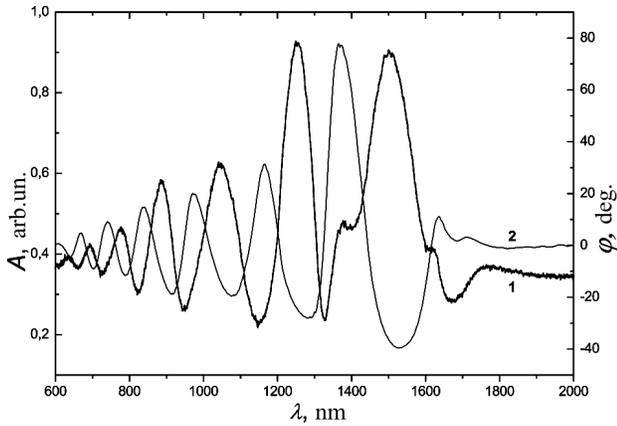
Fig. 1. Piezophotoconductivity amplitude (*1*) and phase shift (*2*) spectra for In_4Se_3 crystal [2]

basis, at proposing a mechanism of spectrum formation for the non-stationary component of the interband absorption coefficient.

2. Layer Shear Deformation. Perturbation Potential

As a result of the anisotropy of chemical bond forces, there emerge specific structural formations in the structure of layered crystals, which look like layers with residual mechanisms of interaction between them. Considering the layered crystals as a system of weakly coupled plane nanostructures, we confine the deformation model of those crystals to that, in which the layers approach one another and shift with respect to one another without substantial changes in their structure. Such a deformation leaves the lattice periodicity in the layer plane (the xy-plane) intact, but brings about considerable variations of the period in the direction normal to the layer plane (the z-axis).

Let the period of the crystal lattice in the non-deformed state be equal to d_z^0 in the z-direction and coincide with the layer thickness. Owing to the pressure action, the adjacent layers become relatively shifted without changing the distance between them. Let the shift l_n occurs along an arbitrary direction in the layer plane, and $l_n < d_{xy}$, where d_{xy} is the lattice period in this direction. In this case, the projection of the lattice period d_z on the normal to the layers changes and equals the period d_z^0 times the number of layers, n, within the period d_{xy},

$$d_z = d_z^0 n. \tag{1}$$

If the ratio $\frac{d_{xy}}{l_n}$ is not integer, the number $n = N\frac{d_{xy}}{l_n}$, where N is the least integer, for which its product with $\frac{d_{xy}}{l_n}$ is an integer number. Hence, owing to the deformation of a layered crystal, which occurs as a relative shift of the layers, there emerges a specific superstructure with the period in the direction normal to the layer plane equal to d_z. The value of this lattice period is a discrete function of the relative shift between the layers, and its minimum variation equals the layer thickness.

The shear deformation of the layers, by changing their equilibrium positions in the undeformed crystal, induces corresponding variations in the electron potential [5, 6]. Bearing in mind the layer structure invariance in the course of this deformation, let us present the potential in the deformed crystal as an imposition of a certain perturbation on the potential of the undeformed crystal. This perturbation arises owing to the deformation-governed spatial redistribution of atoms along the normal to the layer plane. Hence, it is periodic with the period d_z and depends on the coordinate z.

In the case of a deformation under the combined action of external factors–in particular, a constant squeezing of the specimen together with a modulated harmonic pressure of a small amplitude–the perturbing potential is a function of the coordinates and the time. Accordingly, the period of the corresponding perturbation d_z has a harmonic component with the modulation frequency, and it is a periodic discrete function of the time. In this case, the average time interval, within which the period d_z remains constant, is equal to the time interval, within which it increases by d_z^0; hence, it depends on the modulation frequency.

The perturbation potential induced by the mechanical stress and existing in the form of the field periodic in space and time creates conditions for the electron diffraction and can be an effective scattering factor giving rise to definite variations in the energy band structure and in the electron redistribution over the band states. Let us consider those variations as virtual, i.e. as transient at band-to-band transitions, and evaluate their role in the formation of intrinsic light absorption spectra.

3. Modulation of Electron State Structure by Layer Shear Deformation

The relative shift of the layers owing to the residual character of the interaction between them cannot

1160

induce substantial mechanical stresses in the crystal and, therefore, cannot considerably affect the structure of electron states [6,7]. Taking this circumstance into account, let us analyze possible changes in the structure of electron states and in their population occurring owing to the layer shear deformation induced by the combined low-frequency harmonic pressure. Our consideration is confined to the simplest model of bands in the undeformed crystal, in which the parabolic dispersion law is obeyed.

Since the crystal dimensions remain constant in the course of the layer shear deformation, let us present the perturbation potential as a difference between the potentials in the deformed and undeformed crystals. The main property of this perturbation is its periodic dependence on the coordinate z, with the period equal to d_z. Changes in the structure of electron states in the undeformed crystal follow from the interaction between electrons and the periodic one-dimensional perturbation potential generated by the layer shift. On the basis of the results obtained from direct calculations of matrix elements for perturbations induced by constant external pressures, a conclusion can be drawn that the shear deformation of layers practically does not affect the band structure, $\varepsilon_0(\mathbf{k})$, in the undeformed crystal. The main changes concern some separate states, the wave vectors of which have the k_z component multiple of the ratio π/d_z. As a result of the degeneration of those states, the dispersion dependence of the energy on the k_z-component of the wave vector with the magnitude

$$k_z = \frac{\pi}{d_z}g = k_g \quad (g = 0, 1, 2, 3, ...), \tag{2}$$

has discontinuities,

$$\varepsilon(\mathbf{k}) = \varepsilon_0(\mathbf{k}) \pm |V_g|\,\delta_{k_z,k_g}, \tag{3}$$

where V_g is the amplitude of the potential Fourier expansion, and δ_{k_z,k_g} is the Kronecker symbol. Hence, the shear deformation of layers brings about the appearance of specific critical points in the energy band structure, whose positions can be controlled by an external force.

If the deformation is induced by an external force which has a harmonic component with a low frequency Ω and a relatively small amplitude l_0, the vector magnitude q has two components,

$$q = q_s + q_0 \sin(\Omega t), \tag{4}$$

where $q_s = \frac{2\pi}{d_z^0}\frac{l_s}{d_{xy}}$, $q_0 = \frac{2\pi}{d_z^0}\frac{l_0}{d_{xy}}$, and l_s is the relative shift between the layers induced by the constant pressure. Taking this circumstance into account, let us analyze the population dynamics of the given energy level as a result of the shear deformation of layers invoked by a low-frequency harmonic pressure. We suppose that a parabolic dispersion law is obeyed in this band, and the Brillouin zone is a cube with the side $2K_0 = \frac{2\pi}{d_z^0}$.

The redistribution of electrons over the band states results directly from their interaction with the periodic one-dimensional perturbation is characterized by the wave vector with a single component different from zero and is equal to $\frac{2\pi}{d_z}$. Owing to this interaction and in accordance with the quasimomentum conservation law, the component k_z of the electron wave vector changes, so that the normal or Umklapp scattering processes are realized. The latter are known to be an effective factor in the establishment of a quasiequilibrium state in the electron subsystem and can invoke the redistribution of electrons over the energy states.

Consider the dynamics of the population on a completely filled isoenergy surface of radius k, which is realized in the case of the scattering by a perturbation potential with the wave vector q that provides the emergence of Umklapp processes. The number of electrons with the given inverse vector q, which leave this surface, is proportional to the area of a segment with the height $k - \chi$. The vector magnitude, $\chi = K_0 - q$, is equal to the smallest k_z-component of the wave vector, which undergoes the Umklapp process. The reduction in the population on the considered isoenergy surface is partially compensated by transitions of electrons onto it from other energy states. The number of such transitions, which is regulated by the principle of correspondence and the quasimomentum conservation law, provides a certain population S_1 on the considered isoenergy surface

$$S_1 = 2\pi[(\eta - k)^2 - (\eta - k) \times$$

$$\times \sqrt{\eta^2 + \chi^2 - 2\eta k} - k(k - \chi)], \tag{5}$$

where $\eta = 2K_0 - q$. At the given q- and K_0-values, the transitions are completely compensated on the isoenergy surface with the radius $k = \eta/2$. Accordingly, the Umklapp processes result in the population growth for all surfaces with the radii $k > \eta/2$, and
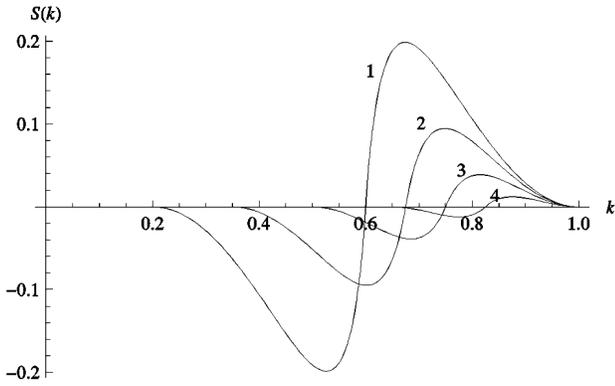
Fig. 2. Dependences of the relative population change of a spherical isoenergy surface on the wave vector for $q_s = = 0.8$ (*1*), 0.65 (*2*), 0.5 (*3*), and 0.65 (*4*)


a

b
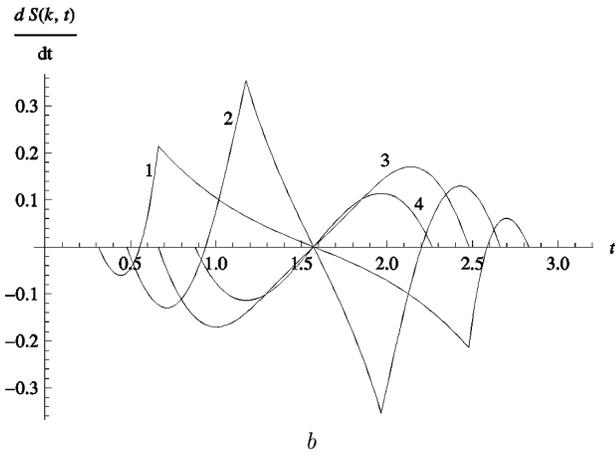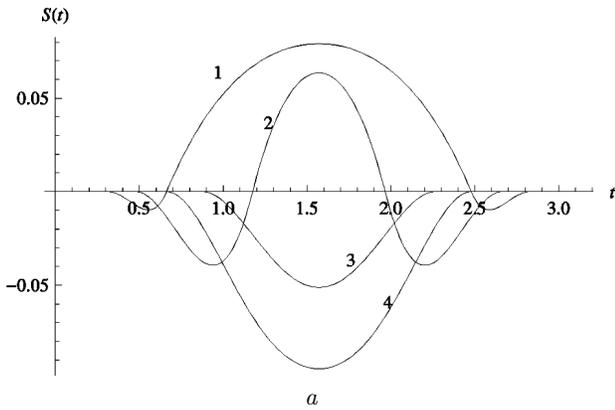
Fig. 3. Time dependences of the relative population change (*a*) and its time derivative (*b*) for $q_s = 0.8$ (*1*), 0.7 (*2*), 0.6 (*3*), and 0.5 (*4*)

the balance between their populations is determined by similar expressions,

$$S_2 = 2\pi \left[(\eta - k)(\eta - k - \chi) - k^2 + k\sqrt{2\eta k + \chi^2 - \eta^2} \right].$$

(6)

The relative change of the state population on a spherical isoenergy surface with an arbitrary radius k as a result of Umklapp processes is described by the equation

$$S(k,t) = 2\pi \Bigg\{ \left[\eta^2 - (2\eta - \chi)k + (k - \eta) \times \right.$$

$$\times \sqrt{\eta^2 + \chi^2 - 2\eta k} \Bigg] \Theta(k - \chi)\left[1 - \Theta(k - \eta/2)\right] +$$

$$+ \left[\eta^2 - \chi\eta - (2\eta - \chi)k + k\sqrt{2\eta k + \chi^2 - \eta^2} \right] \times$$

$$\times \Theta(k - \eta/2)\left[1 - \Theta(k - k_0)\right] \Bigg\},$$

(7)

where the Heaviside functions $\Theta(k)$ are used to confine the corresponding intervals of wave vectors. In Fig. 2, the dependences of the relative change of the isoenergy surface population on the wave vector magnitude are exhibited for some q_s-values.

Hence, the Umklapp processes result in the establishment of a certain balance between the populations of electron states on the isoenergy surfaces, which is determined by their radii k. In this case, the relative change in the population of isoenergy surfaces depends on the time and, as follows from expression (7), is a complicated periodic function of this quantity. A specific form of this dependence is determined by the ratio between the radius of the spherical isoenergy surface and the amplitude of the vector q. In Fig. 3, the time dependences of the relative populations on various isoenergy surfaces and their derivatives with respect to the time are depicted for the given amplitudes of the harmonic component of the vector q_0.

4. Non-Stationary Component of the Interband Absorption Coefficient

Now let us proceed to the evaluation of the spectrum for the non-stationary component of the interband light absorption coefficient, which arises owing to the low-frequency shear deformation of layers. We will confine the consideration to a simple band structure

in the undeformed crystal, which is not crucial for this evaluation, and neglect the intensity of inverse interband transitions. A direct origin of changes in the coefficient of interband light absorption in the undeformed crystal under the conditions concerned is the emergence of specific critical points in the band structure and the redistribution of electrons over the states of those bands. These variations, which are associated with the mechanical stress arising in the crystal as a result of the shift of layers and which are realized in the form of consecutive short pulses, are considered here as virtual ones [8], i.e. transient at interband transitions.

In the framework of the model proposed, the number of interband transitions occurring per unit time is a result of two processes: quantum-mechanical transitions of valence electrons at a constant rate and a slow classical process, which governs a time variation in the number of electrons capable of such transitions. Accordingly, taking the structure of $S(k,t)$ into account, the coefficient of light absorption $\alpha(\omega, t)$ at the frequency ω can be written down in the form

$$\alpha(\omega, t) = C \int W_0(k) \left[1 + S(k,t) + \Delta t_i \frac{\partial S(k,t)}{\partial t} \right] d\tau_k, \tag{8}$$

where $W_0(k)$ is the probability of interband transitions, Δt_i are time intervals within which $S(k,t) \neq 0$, and C is a constant.

The non-stationary component of the absorption coefficient,

$$\alpha_s(\omega, t) = C \int W_0(k) \left[S(k,t) + \Delta t_i \frac{\partial S(k,t)}{\partial t} \right] d\tau_k, \tag{9}$$

has a rather complicated time dependence, which is associated with the presence of the time-dependent term $\left[S(k,t) + \Delta t_i \frac{\partial S(k,t)}{\partial t} \right]$ substantially affecting its dependence on the light quantum energy. From the viewpoint of practical interest, the harmonic components of the function $\alpha_s(\omega, t)$, in particular, the structure of their spectra, are of value. By expanding the time-dependent term $\left[S(k,t) + \Delta t_i \frac{\partial S(k,t)}{\partial t} \right]$ in the Fourier series, we obtain expressions for the amplitudes of orthogonal components of the harmonic with the frequency Ω.

As follows from the structure of the time-dependent factor, the amplitude of the in-phase component

$\mathcal{I}_s(k)$ does not depend on the rate of population variation and, accordingly, can be presented as a sum of integrals $\mathcal{I}_{s_i}(k)$,

$$\mathcal{I}_s = \frac{1}{\pi} \sum_i \int_{\theta_{0i}}^{\theta_{mi}} S(k,\theta) \sin(\theta) \, d\theta, \tag{10}$$

where the limits θ_{0i} and θ_{mi} determine intervals within the range $[0, 2\pi]$, in which the quantity $S(k,t) \neq 0$ and has a corresponding functional dependence on the time for the given wave vector k. The amplitude of the harmonic shifted by $\pi/2$ is calculated as the average value of corresponding integrals,

$$\mathcal{I}_{as}(k) = \frac{1}{\pi} \sum_i \theta_i(k) \int_{\theta_{0i}}^{\theta_{mi}} \frac{\partial S(k,\theta)}{\partial \theta} \cos(\theta) \, d\theta, \tag{11}$$

where $\theta_i(k)$ is the corresponding angle within the given integration limits. In view of the following equality, which is valid in the considered integration limits,

$$\Omega \int_{\theta_{0i}}^{\theta_{mi}} S(k,\theta) \sin(\theta) \, d\theta = \int_{\theta_{0i}}^{\theta_{mi}} \frac{\partial S(k,\theta)}{\partial \theta} \cos(\theta) \, d\theta, \tag{12}$$

let us write down $\mathcal{I}_{as}(k)$ in the form

$$\mathcal{I}_{as}(k) = \sum_i \Omega \theta_i(k) \mathcal{I}_{si}(k). \tag{13}$$

Notice that, owing to the irrationality of some terms in the integrands, integrals (10) and (11) include terms in the form of elliptic integrals [9].

The integration of expression (9) making allowance for the dependence of the quantities $\mathcal{I}_s(k)$ and $\mathcal{I}_{as}(k)$ on the wave vector and the type of optical transitions allows the Ω-harmonic of the non-stationary absorption coefficient to be presented in the form

$$\alpha(\omega) = \alpha_s^0(\omega_g) \sin(\Omega t + \varphi), \tag{14}$$

where $\omega_g = \frac{1}{\hbar}(\hbar\omega - E_g - 2V_g)$, $\tan \varphi = \frac{\mathcal{I}_s(\omega_g)}{\mathcal{I}_{as}(\omega_g)}$, and E_g is the energy gap width. Hence, the structure of the spectrum of the non-stationary absorption coefficient component is formed by the corresponding changes in the energy band structure of the undeformed crystal and the Umklapp processes connected with the

shear deformation of layers. Concerning the structure of this component, the non-trivial dependence of the phase shift on the energy of light quanta, $\varphi(\omega)$, has primary importance. In essence, the energy dependence of the phase shift on the quantum energy, $\varphi_k(\omega)$, reflects a complicated dynamics of the energy level population, which the Umklapp processes are responsible for.

Hence, the spectral structure of the orthogonal components of the $\alpha_s(\omega)$ harmonic– the in-phase, $\alpha_s^{\mathrm{I}}(\omega_g)$, and phase-shifted, $\alpha_s^{\mathrm{II}}(\omega_g)$, ones–stems from the functional dependence of the amplitude $\alpha_s^0(\omega)$ and the phase $\varphi_k(\omega_g)$ on the quantum energy. By presenting them in the form

$$\alpha_s^{\mathrm{I}} = \alpha_s^0 \cos(\varphi), \quad \alpha_s^{\mathrm{II}} = \alpha_a^0 \sin(\varphi), \tag{15}$$

we note that this relation between the spectra of orthogonal components was obtained experimentally for the in-phase and phase-shifted components of the piezophotoconductivity in In_4Se_3 crystals [3].

5. Conclusion

The model proposed for the formation of the spectrum of the non-stationary absorption coefficient component is based on a comparison between the electron band structures in deformed and undeformed crystals. The shear deformation of layers is supposed to be a crucial factor giving rise to certain changes in the structure of electron states. Its action is equivalent to a variation of the lattice period along the normal to the layer plane. Modifications induced by mechanical stresses in the electron state structure of layered crystals are insignificant, being blocked by fundamental electronic properties of the crystal. Those modifications, which manifest themselves in the form of jumps in the dispersion dependence of the energy on the wave vector, the k_z-component of which is a multiple of the ratio π/d_z, reveal themselves as special points in the combined density of states. Accordingly, they can be explicitly observed in the structure of interband absorption spectra; first of all for such crystals, in which the layer stacks have rather a large thickness. The experimental identification of those features demands that techniques similar to modulation spectroscopy [10, 11] should be applied. The researches of piezophotoconductivity, as an analog of the modulation spectroscopy of photoconductivity,

cover a wide scope of physical processes and, therefore, may turn out an effective method of investigation dealing with the electronic properties of layered semiconductors.

1. Y.M. Stakhira and R.Y.Stakhira, Zh. Fiz. Dosl. **2**, 3 (1998).
2. Y.M. Stakhira, R.Y. Stakhira, and V.P. Savchyn, Ukr. Fiz. Zh. **50**, 6 (2005).
3. Y. Stakhira and R. Stakhira, J. Phys. Stud. **11**, 2 (2007).
4. R.Y. Stahira, G.D. Danylyuk, and Ya.M. Fiyala, Novi Tekhnol. **27**, 1 (2010).
5. M. Sznajder, K. Rushchanskii, L. Kharkhalis *et al.*, Phys. Status Solidi B **243**, 592 (2006).
6. D.M. Bercha, K. Rushchanskii, I.V. Slipukhina *et al.*, Cond. Matt. Phys. **229**, 6 (2003).
7. M.S. Brodin and I.V. Blonsky, *Excitonic Processes in Layered Crystals* (Naukova Dumka, Kyiv, 1986) (in Russian).
8. L.I. Schiff, *Quantum Mechanics* (McGraw Hill, New York, 1968).
9. *Handbook of Mathematical Functions*, edited by M. Abramovitz and I.A. Stegun (Dover, New York, 1970).
10. R. Sensarma, K. Sengupta, and S. Das Sarma, Phys. Rev. B **84**, 8 (2011).
11. A. Tokuno and T. Giamarchi, e-print arXiv:1101.2469v2 (2011).

Й.М. Стахіра, Р.Й. Стахіра

МЕХАНІЗМ ФОРМУВАННЯ СПЕКТРІВ НЕСТАЦІОНАРНОЇ П'ЄЗОФОТОПРОВІДНОСТІ ШАРУВАТИХ КРИСТАЛІВ

Р е з ю м е

Проаналізовано зміни у структурі електронних станів шаруватих кристалів, які зумовлені деформацією зсуву шарів, що здійснюється модульованим низькою частотою зовнішнім тиском. Показано, що така деформація приводить до виникнення надструктури, період якої у напрямку, нормальному до площини шарів, рівний цілому числу товщин шару. Встановлено, що взаємодія електронів з деформаційно збуреним потенціалом приводить до виникнення розривів у дисперсійній залежності енергії від хвильового вектора, які регулярно розміщені по його величині. Показано, що ця взаємодія спричинює перерозподіл електронів по станах у зонах, який реалізується процесами перекидання. Запропоновано рівняння балансу заселеності станів, проаналізовано його динаміку. Проведено оцінку нестаціонарної складової коефіцієнта міжзонного поглинання. Показано, що спектр цієї складової має смугастий характер, а фаза гармоніки модуляційної частоти зміщена відносно фази тиску на величину кута, який залежить від енергії кванта світла.