

Theoretical treatment of the resonant hyper-Raman scattering of light in crystals

L.E.Semenova, K.A.Prokhorov

A.Prokhorov General Physics Institute, Russian Academy of Sciences,
38 Vavilov St., 119991 Moscow, Russia

The work is aimed at discussion of different mechanisms of the resonant hyper-Raman scattering of light with participation of excitons in semiconductor crystals and analysis of their contributions to the scattering intensity.

Работа посвящена обсуждению различных механизмов резонансного гиперкомбинационного рассеяния света с участием экситонов в полупроводниковых кристаллах и анализу их вкладов в интенсивность рассеяния.

The Raman scattering (RS) of light is one of important investigation techniques of semiconductor crystals for a long time. Of special interest is the resonant Raman scattering (RRS) where the incident or scattered frequency is close to the resonance with fundamental electronic transitions, since the RRS makes it possible to obtain information on excitations in semiconductors and their interactions [1]. The hyper-Raman scattering (HRS) of light is a non-linear optical process where the simultaneous absorption of two incident photons is accompanied by creation of phonon and emission of scattered photon [2]. Along with the RRS, of a particular interest is the resonant hyper-Raman scattering (RHRS) where the doubled energy of exciting radiation is close to the energy gap. For the RHRS, two-photon allowed transitions can be in resonance with exciting radiation, i.e. in the case of HRS, other intermediate states are involved in the scattering process. This results in new features in hyper-Raman spectra. Thus, the HRS provides an additional information on different excitations in semiconductors.

Experimental investigations of the RHRS in a number of semiconductor crystals were reported in [3–9]. In the work by Garsia-Cristobal et al. [10], the RHRS mediated by dipole-allowed Fröhlich interaction was theoretically studied and the hyper-Raman

efficiency was calculated taking into account excitonic effects. Theoretical analysis of some RHRS mechanisms has been performed for a CdS crystal [11–13]. The different scattering mechanisms for RHRS were considered and the expressions for their contributions to the cross-section were derived in [14]. The present work is aimed at the discussion of features of the RHRS on optical phonons under involvement of excitons.

As mentioned above, in the HRS process, a phonon arises and scattered photon is emitted due to absorption of two incident photons, i.e. the HRS changes the vibrational state of a crystal, but the electronic state remains unchanged, although the virtual intermediate states are excited. We assume that the intermediate states of electronic system are the electron-hole pairs bound by the Coulomb interaction, i.e. the Wannier excitons.

In this case, the HRS event is described by the following sequence of processes: (1) a transition of electronic system from the ground state to an excitonic state when the incident photon with frequency ω_L , polarization ε_L and wave vector \mathbf{q}_L is absorbed; (2) a transition between excitons under absorption of another photon of exciting radiation; (3) creation of a phonon with frequency ω_P and wave vector \mathbf{q}_P due to exciton-lattice interaction; (4) annihilation of

an exciton accompanied by the of scattered photon (ω_S , ϵ_S , \mathbf{q}_S) emission. The first-order HRS (i.e. one-phonon scattering) is described in the fourth order of the perturbation theory and its differential cross-section can be written as [14]

$$\frac{d\sigma}{d\Omega} = \frac{2\pi\hbar e^6 \eta_S \omega_S^2 (n_P + 1)}{m^6 c^4 \eta_L^2 \omega_L^2} N_L V |\epsilon_\gamma^S \epsilon_\beta^L \epsilon_\alpha^L \beta_{\alpha\beta\gamma} (2\mathbf{q}_L - \mathbf{q}_S)|^2, \quad (1)$$

where e and m are electron charge and mass, respectively; c is the light speed, n_P is the number of phonons; V is the crystal volume; $N_L = n_L/V$ is the photon density of incident radiation; $\eta_L(\eta_S)$ is the refractive index for the frequency $\omega_L(\omega_S)$. The HRS tensor $\beta_{\alpha\beta\gamma}(\mathbf{q})$ has the form [14],

$$\beta_{\alpha\beta\gamma}(\mathbf{q}) = \sum_{\Lambda_1 \Lambda_2 \Lambda_3} \frac{\Pi_{\Lambda_3}^{\gamma} P_{\Lambda_3 \Lambda_2} \Pi_{\Lambda_2 \Lambda_1}^{\beta} \Pi_{\Lambda_1 0}^{\alpha}}{(E_{\Lambda_3} - \hbar\omega_S)(E_{\Lambda_2} - 2\hbar\omega_L)(E_{\Lambda_1} - \hbar\omega_L)}, \quad (2)$$

where the index $\Lambda = (c\nu\lambda)$ corresponds to the excitonic state formed due to the Coulomb interaction of electron from the conduction band c and a hole from the valence band ν . $\lambda = (\zeta lm)$ denotes a set of quantum numbers associated with a relative electron-hole motion; the main quantum number ζ coincides with n for the discrete spectrum or with k for the continuous spectrum. E_Λ is the energy of corresponding intermediate excitonic state in the Brillouin zone center. (We assume that the scattering process occurs in the Brillouin zone center due to small values of photon wave vectors). $\Pi_{\Lambda 0}^\alpha$ describes the dipole transition from the ground state to an excitonic state [15]

$$\Pi_{\Lambda 0}^\alpha = \left\{ \pi_{c\nu}^\alpha - M_{c\nu}^{\alpha\alpha} p_\alpha \right\} \chi_{c\nu}^\lambda(\mathbf{r})^* \Big|_{r=0}, \quad (3)$$

where $\hat{p}_\alpha = -i\hbar\partial/\partial r_\alpha$; $\pi_{c\nu}$ is the interband matrix element of the momentum operator; $\chi_{c\nu}^\lambda(\mathbf{r})$ is the hydrogen-like wave function of relative electron-hole motion. Here the first term in the curly brackets describes the allowed dipole transition to a s -excitonic state (with the orbital quantum number $l = 0$). The second term corresponds to another type of dipole transitions which are weakly-forbid-

den and cause excitation of p -excitons ($l = 1$). The parameter $M_{c\nu}^{\alpha\alpha}$ is defined in [15].

$\Pi_{\Lambda'\Lambda}^\beta$ describes the transitions between excitonic states Λ' and Λ [16]

$$\Pi_{\Lambda'\Lambda}^\beta = \left[\pi_{c'c}^\beta \delta_{\nu'\nu} - \pi_{\nu'\nu}^\beta \delta_{c'c} \right] \langle \chi_{c'\nu'}^\lambda | \chi_{c\nu}^\lambda \rangle + \delta_{\nu'\nu} \delta_{c'c} \left[M_{c'c}^{\beta\beta} - M_{\nu'\nu}^{\beta\beta} \right] \langle \chi_{c'\nu'}^\lambda | \hat{p}_\beta | \chi_{c\nu}^\lambda \rangle. \quad (4)$$

In expression (4), the first term corresponds to transitions between excitonic states belonging to different pairs of bands (interband transitions), whereas the second term describes the intraband dipole transitions between excitonic states.

$P_{\Lambda'\Lambda}$ describes the transition between excitonic states Λ' and Λ due to interaction with phonons. In the zero wave vector approximation which commonly is used for a first-order scattering the matrix element $P_{\Lambda'\Lambda}$ is given by [17]

$$P_{\Lambda'\Lambda} \approx \gamma_D \left\{ \Xi_{c'c} \delta_{\nu'\nu} - \Xi_{\nu'\nu} \delta_{c'c} \right\} \langle \chi_{c'\nu'}^\lambda | \chi_{c\nu}^\lambda \rangle \quad (5)$$

for the deformation potential interaction typical of all optical phonons or

$$P_{\Lambda'\Lambda} \approx \gamma_F \left\{ \hat{\mathbf{q}} \cdot \mathbf{r}_{c'c} \delta_{\nu'\nu} - \hat{\mathbf{q}} \cdot \mathbf{r}_{\nu'\nu} \delta_{c'c} \right\} \langle \chi_{c'\nu'}^\lambda | \chi_{c\nu}^\lambda \rangle + \gamma_F \delta_{\nu'\nu} \delta_{c'c} \langle \chi_{c'\nu'}^\lambda | \hat{\mathbf{q}} \cdot \mathbf{r} | \chi_{c\nu}^\lambda \rangle \quad (6)$$

for the Fröhlich interaction which contributes to a scattering by longitudinal optical (LO) phonons only. Here γ_D is constant associated with the relative displacement of atoms in the unit cell and $\Xi_{n'n}$ is the deformation potential; γ_F is the constant of the Fröhlich interaction and $\hat{\mathbf{q}}$ is the unit vector in the direction \mathbf{q}_p . It is seen from the expression (6) that the Fröhlich interaction induces both the interband (first term) and intraband (second term) transitions between excitonic states.

Now the HRS process will be considered for the case when the doubled frequency of incident radiation (or the scattered light frequency) is close to the energy gap width ($2\hbar\omega_L$, $\hbar\omega_S \sim E_{c\nu}$), hence, the non-resonance contributions will be neglected.

The Fröhlich scattering mechanism, to which a sequence of intermediate states, s - p - s , corresponds, is known to play a leading role in the RHRS [10]. As is seen from the expression (3), absorption of incident photon is accompanied by transition to an s -exciton state under condition that the dipole transition is allowed ($\pi_{c\nu} \neq 0$). Then the second photon can induce the interband transi-

tion to *s*-exciton belonging to another pair of bands or the intraband dipole transition to a *p*-exciton. Under resonance conditions, it is just the latter that is of interest. In this case, the deformation potential and interband Fröhlich interactions result in transitions to *p*-exciton states. Whereas the intraband Fröhlich coupling causes a transition to an *s*-exciton belonging to same pair of bands. But the transition from the *p*-excitonic state to the ground one is a process of higher order as compared to the ordinary dipole transition and its oscillator force is significantly less than that for the transition to *s*-excitonic state. Thus, the HRS process via the intraband Fröhlich scattering is predominant.

To evaluate the corresponding hyper-Raman tensor, it is necessary to calculate the exciton-photon and exciton-phonon matrix elements and to sum over all intermediate excitonic states of discrete and continuous spectra. The HRS efficiency was evaluated by this approach in [10]. The expression obtained is, however, too cumbersome. In our work [14], the HRS tensor describing the contribution of the considered scattering mechanism was calculated by applying the Green's function method and has a form

$$\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q}) = i \frac{2\hbar\gamma_F\pi_{vc}^\gamma\pi_{cv}^\alpha[M_{cc}^{\beta'\beta} - M_{vv}^{\beta'\beta}]\hat{q}_{\beta'}}{3\pi R^3 a^3} \kappa_L^2 \kappa_S^4 \times \left\{ \sum_{n=2}^{\infty} \frac{n^2 - 1}{n^5} \frac{J_5(n, \kappa_S) J_4(n, \kappa_L)}{\xi(\omega_L) - n^{-2} - i\gamma_n} + \int_0^{\infty} \frac{k(1+k^2)}{1 - \exp(-2\pi/k)} \frac{J_5(i/k, \kappa_S) J_4(i/k, \kappa_L)}{\xi(\omega_L) + k^2 - i\gamma_k} dk \right\} \quad (7)$$

in the approximation of the zero phonon wave vector. Here *R* and *a* are the binding energy and the radius of exciton, respectively; γ_n is the exciton damping. The parameters $\xi(\omega)$ and κ_L are defined as $\xi(\omega) = (E_{cv} - 2\hbar\omega/R)$ and $\kappa_L = \sqrt{R/(E_{cv} - \hbar\omega_L)}$. Hereafter, the indices *L* and *S* correspond to the incident and scattered light, respectively. The integrals $J_4(n, \kappa)$ and $J_5(n, \kappa)$ are defined by the expressions (30) and (40) in [14].

Taking into account only the dipole-allowed transitions, another scattering mechanism can be considered which shows the resonance increase when the photon energy of scattered light is close to the 1*S*-exciton energy. This HRS process is described

by the following sequence of transitions: (1) transition from the ground states to an *s*-exciton composed of electron from the lowest conduction band *c* and the hole from the highest valence band *v*; (2) transition of the electron to the higher conduction band *c'* or the hole to the lower valence band *v'*; (3) transition of the electron between the conduction bands *c'* and *c* or the hole between the valence bands *v'* and *v* due to exciton-lattice coupling; (4) return of electronic system to the ground state.

Under the assumption of the same parameters of excitons belonging to different pairs of bands, the corresponding tensor is given as

$$\beta'_{\alpha\beta\gamma}(\mathbf{q}) = \frac{\gamma\pi_{vc}^\gamma\pi_{cv}^\alpha}{\pi R^2 a^3} \kappa_L^2 \kappa_S^2 \times \left\{ \sum_{c'v'} [\Theta_{cc'}\delta_{vv'} - \Theta_{v'v}\delta_{cc'}] [\pi_{cc'}^\beta\delta_{vv'} - \pi_{v'v'}^\beta\delta_{cc'}] \times \sum_{n=1}^{\infty} \frac{1}{n^3} \frac{\tilde{J}(n, \kappa_S)\tilde{J}(n, \kappa_L)}{E_{c'v'} - R/n^2 - 2\hbar\omega_L} + \int_0^{\infty} \frac{k}{1 - \exp(-2\pi/k)} \frac{\tilde{J}(i/k, \kappa_S)\tilde{J}(i/k, \kappa_L)}{E_{c'v'} + Rk^2 - 2\hbar\omega_L} dk \right\}, \quad (8)$$

where $\tilde{J}(n, \kappa) = (1 - (\kappa/n)^2)^{-1}$, parameters γ and $\Theta_{nn'}$ coincide with γ_D and $\Xi_{nn'}$ for the deformation potential interaction or with γ_F and $\hat{q}_j r_{nn'}^j$ for the Fröhlich scattering. The HRS event described by the expression (8) includes transitions to higher-lying conduction bands and to deeper valence bands. Therefore, its contribution is considerably smaller than that of the intraband Fröhlich scattering mechanism which is described in the framework of the two-band model ($\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})$).

Although $\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})$ decreases more fastly than $\beta'_{\alpha\beta\gamma}(\mathbf{q})$ as the incident frequency deviates away from the two-photon resonance, our estimations show that $\beta'_{\alpha\beta\gamma}(\mathbf{q})$ is negligible in comparison with $\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})$ far away from the resonance, too.

If in a semiconductor the selection rules allow the two-photon transition between the highest valence band and the lowest conduction band along with the one-photon dipole transition, the additional scattering mechanisms which include the two-photon transitions in *s*-excitonic states can be involved in the HRS process. As is seen from the ex-

pressions (5) and (6), the interband Fröhlich and deformation potential interactions cause then transitions to *s*-excitons belonging to other pair band ($\beta_{\alpha\beta\gamma}^{(3)}(\mathbf{q})$) and the intraband Fröhlich interaction results in the transition to *p*-exciton ($\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})$). These scattering mechanisms were considered in detail in [14]. By using the Green's function formalism, the expressions for the corresponding HRS tensors, $\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})$ and $\beta_{\alpha\beta\gamma}^{(3)}(\mathbf{q})$, were also obtained [14]. Besides, the mechanism of the forbidden Fröhlich HRS ($\beta_{\alpha\beta\gamma}^f(\mathbf{q})$) is worth to take into account which is described as follows: the two-photon transition to an *s*-exciton state and then the intraband transition between *s*-excitons due to the *q*-dependent Fröhlich interaction which is forbidden in the zero wave vector approximation.

Thus, various scattering mechanisms corresponding to different sequences of intermediate states contribute to the HRS if both the one-photon and two-photon transitions are allowed in a semiconductor. But it is obvious that the HRS described by $\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})$ is dominant because it is described in the framework of the two-band model and includes only the dipole-allowed transitions, unlike other scattering mechanisms.

However, it should be noted that the resonance conditions for $\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})$, $\beta_{\alpha\beta\gamma}^{(3)}(\mathbf{q})$ and $\beta_{\alpha\beta\gamma}^f(\mathbf{q})$ are established when the doubled energy of exciting radiation quantum is close to the energy level of the 1*S* exciton ($2\hbar\omega_L \approx E_{1S}$). Whereas the resonance for $\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})$ takes place when $2\hbar\omega_L \approx E_{2P}$. Therefore, other scattering mechanisms can be non-negligible. Our estimations have shown that close to two-photon resonance with the 1*S* exciton, the contribution of the HRS caused by the forbidden Fröhlich scattering can be comparable with that of the HRS described by $\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})$ if the effective masses of electron and hole differ considerably from one another [14]. As a result, the frequency dependence of the HRS intensity can contain a singularity at $2\hbar\omega_L \approx E_{1S}$.

Moreover, $\beta_{\alpha\beta\gamma}^{(1)}(\mathbf{q})$ depends on the incident polarization. By using the *f*-sum rule, the difference $[M_{cc}^{\beta\beta} - M_{vv}^{\beta\beta}]$ can be expressed via effective masses of electron m_e^* and hole m_h^*

$$[M_{cc}^{\beta\beta} - M_{vv}^{\beta\beta}] = m[1/m_{e\beta}^* + 1/m_{h\beta'}^*]. \quad (9)$$

The effective mass is generally the tensor value but its non-diagonal components are zero for a number of crystals. Because of this, the expression (9) can be changed by $[M_{cc}^{\beta\beta} - M_{vv}^{\beta\beta}] = m/\mu\delta_{\beta\beta}$ where μ is the reduced mass of exciton. In this case, the hyper-Raman scattering mechanism described by the expression (7) contributes to the HRS intensity only under condition that the exciting radiation polarization lies in a plane formed by photon wave vectors ($q_\beta \neq 0$). Unfortunately, the measurements of the HRS polarization dependences close to the two-photon resonance with the 2*p* exciton state, to our knowledge, are absent except for the investigations in a thin film ZnSe sample on GaAs substrate [7].

Therefore, in a scattering geometry where $q_\beta = 0$, other HRS mechanisms contribute to the hyper-Raman intensity. In this case, obviously, it is just the RHRS due to the two-photon transition to a *s*-excitonic state that dominates. Such HRS seems to be similar to the RRS. But the HRS spectra for $2\hbar\omega_L \sim E_{1S}$ can differ considerably from the RRS spectra for $\hbar\omega_L \sim E_{1S}$. It is known from the theory of two-photon absorption [16] that the two-photon transition to a *s*-exciton can be described in terms of the two-band model where the absorption of incident photon is accompanied by excitation of *p*-exciton and another photon induces the intraband transition to an *s*-exciton. The two-photon excitation of a *s*-exciton can be due also to the transitions to the higher-lying conduction band *c'* or the lower valence band *v'* (three-band model). In other words, initially the transition to the *s*-exciton belonging to *c'* and *v* bands or to *c* and *v'* ones occurs, then the interband transition of an electron or hole takes place. Thus, both the two-band and three-band models contribute to the HRS mechanisms considered. Since their contributions are opposite in sign [14], their interference can result in additional singularities in HRS spectra and to a more complex resonance profile.

In order to evaluate the role of the scattering mechanism described by $\beta'_{\alpha\beta\gamma}(\mathbf{q})$, the tensors $\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})$, $\beta_{\alpha\beta\gamma}^{(3)}(\mathbf{q})$ and $\beta'_{\alpha\beta\gamma}(\mathbf{q})$ were calculated in a wide frequency range for the Fröhlich interaction only. The results are presented in Fig. 1. As is seen from the Figure, $\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})$ dominates over $\beta_{\alpha\beta\gamma}^{(3)}(\mathbf{q})$ and $\beta_{\alpha\beta\gamma}^{(4)}(\mathbf{q})$ near two-photon resonance, but

$\beta'_{\alpha\beta\gamma}(\mathbf{q})$ becomes comparable with $\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})$ far from the resonance.

To conclude, in general case, various scattering mechanisms are involved in the HRS process. Their contributions are defined by the symmetry and parameters of crystal as well as by the scattering geometry and depend on incident frequency. Thus, investigations of the hyper-Raman scattering close to the two-photon resonance with excitonic levels are of interest because the analysis of resonance profiles allows one to obtain additional information on the semiconductor.

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References

1. R.M.Martin, L.M.Falikov, in: Light Scattering in Solids, ed. by M.Cardona, Springer, Berlin (1975).
2. D.A.Long, L.Stanton, *Proc. Roy. Soc. A*, **318**, 441 (1970).
3. Yu.N.Polivanov, R.Sh.Sayakhov, *Pis'ma Zh. Eksp. Teor. Fiz.*, **30**, 617 (1979).
4. V.A.Maslov, K.K.Ondriash, Yu.N.Polivanov et al., *Las. Phys.*, **6**, 132 (1996).
5. K.Inoue, K.Watanabe, *Phys. Rev. B*, **39**, 1977 (1989).
6. K.Watanabe, K.Inoue, F.Minami, *Phys. Rev. B*, **46**, 2024 (1992).
7. K.Inoue, F.Minami, Y.Kato, K.Yoshida, *J. Cryst. Growth.*, **117**, 738 (1992).
8. S.Kono, N.Naka, M.Hasuo et al., *Solid State Commun.*, **97**, 455 (1996).
9. L.Filipchiclis, H.Siegle, A.Hoffmann, C.Thomson, *Phys. Stat. Solidi B*, **212**, R1 (1999).
10. A.Garcia-Cristobal, A.Cantarero, C.Trallero-Ginner, M.Cardona, *Phys. Rev. B*, **58**, 10443 (1998).
11. L.E.Semenova, K.A.Prokhorov, in: Proc. of XVIth Intern. Conf. Raman Spectroscopy

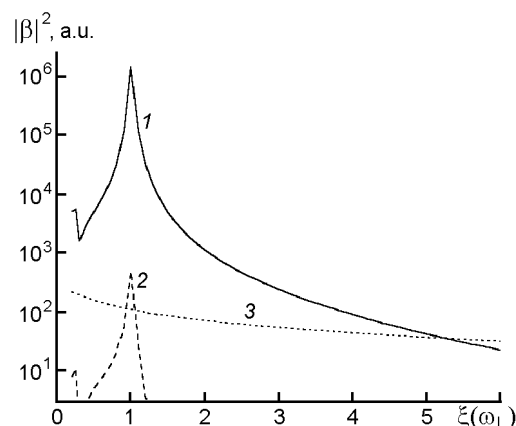


Fig. 1. The contributions of three possible scattering mechanisms described by the hyper-Raman tensors $|\beta_{\alpha\beta\gamma}^{(2)}(\mathbf{q})|^2$ (1), $|\beta_{\alpha\beta\gamma}^{(3)}(\mathbf{q})|^3$ (2), and $|\beta'_{\alpha\beta\gamma}(\mathbf{q})|^2$ (3) as a function of parameter $\xi(\omega_L) = (E_{cv} - 2\hbar\omega_L)/R$. When calculating, the typical parameters of semiconductors crystals were used: $R = 0.01E_{cv}$, $\hbar\omega_p = 1.5R$ and $\gamma = 0.03$. Besides, the virtual transition to the only one higher-lying conduction band c' ($E_{c'c} = 1.5E_{cv}$) was taken into account.

- (Cape Town, 1998), John Wiley & Sons, Chichester (1998), p.120.
12. L.Semenova, K.Prokhorov, *Proc. SPIE*, **3734**, 207 (1999).
13. L.Semenova, K.Prokhorov, *Proc. SPIE*, **4069**, 190 (2000).
14. L.E.Semenova, K.A.Prokhorov, *Zh. Eksp. Teor. Fiz.*, **123**, 1048 (2003).
15. M.M.Denisov, V.P.Makarov, *Phys. Stat. Solidi B*, **56**, 9 (1973).
16. K.Rustagi, F.Pradere, A.Mysyrowicz, *Phys. Rev. B*, **8**, 2721 (1973).
17. R.M.Martin, *Phys. Rev. B*, **4**, 3676 (1971).

Теоретичне трактування резонансного гіперкомбінаційного розсіяння світла у кристалах

Л.Є.Семенова, К.О.Прохоров

Роботу присвячено обговоренню різних механізмів резонансного гіперкомбінаційного розсіяння світла за участю екситонів у напівпровідникових кристалах та аналізу їх внесків в інтенсивність розсіяння.