Optical anisotropy of many-valley cubic semiconductors

E. G. Tsitsishvili

M. V. Lomonosov State University, Moscow

(Submitted 3 January 1985)
Zh. Eksp. Teor. Fiz. **89**, 550–555 (August 1985)

A calculation is made of the birefringence induced by spatial dispersion in cubic crystals with a many-valley structure of the conduction band in the wavelength range of indirect exciton transitions. The effect is due to the nonsphericity of the energy spectrum of the conduction band and is governed by the anisotropy constants of the phonon spectrum.

An allowance for the spatial dispersion of the permittivity gives rise to an optical anisotropy of cubic crystals.[1] In the case of nongyrotropic semiconductors in their transparency range this optical anisotropy is manifested by a birefringence. In the case of direct-gap semiconductors the birefringence in the region of interband (or exciton) transitions is due to a nonsphericity (corrugations) of the energy spectrum of the valence band which is characteristic of cubic crystals. The wave functions of the valence band quadruply degenerate at the point $\mathbf{k}=0$ depend on the direction of quasimomentum $\mathbf{k}$, so that interband matrix elements of the electron-photon interaction operator (considered for a fixed value of $\mathbf{k}$) exhibit a polarization dependence. When there is in the momentum space a preferred direction selected by the wave vector of light $\mathbf{q}$, the dependence of the matrix elements on the direction of polarization of light gives rise to an anisotropy of the permittivity tensor.[2]

In the case of some cubic semiconductors the lower minimum of the conduction band is not located at the center of the Brillouin zone but on [100] or [111] axes. The fundamental absorption edge of such semiconductors corresponds to indirect exciton transitions. The many-valley structure of the conduction band gives rise to a polarization dependence of the corresponding matrix elements. Therefore, we can expect the nonsphericity of the conduction band to be also a cause of optical anisotropy.

We shall calculate the birefringence of cubic crystals with a many-valley structure of the conduction band in the vicinity of the ground state of indirect excitons.

According to the phenomenological analysis in Ref. 1, a birefringence occurs in particular when light propagates along the [110] crystallographic direction. The magnitude of the effect is then given by the expression

$$2n_0\Delta n=\Delta\varepsilon(\omega,\mathbf{q})=\varepsilon_{xx}(\omega,\mathbf{q})-\varepsilon_{xy}(\omega,\mathbf{q})-\varepsilon_{zz}(\omega,\mathbf{q}), \qquad (1)$$

where ε_{ij} are the components of the permittivity tensor in a system of [100] fourfold axes.

The permittivity tensor is given by[1]

$$\varepsilon_{ij}(\omega,\mathbf{q})=\varepsilon_{ij}^{(0)}(\omega)-\frac{4\pi}{\omega^2 V}\sum_f \frac{\langle 0|M^i(\mathbf{q})|f\rangle\langle f|M^j(-\mathbf{q})|0\rangle}{\hbar\omega-E_f}, \qquad (2)$$

where V is the volume of a crystal and $\varepsilon_{ij}^{(0)}(\omega)$ is the background permittivity dependent smoothly on the frequency of light ω. The matrix element for indirect transitions is given by[3]

$$\langle 0|M^i(\mathbf{q})|f\rangle=\sum_v \frac{\langle 0|e^{i\mathbf{q}\mathbf{r}}j^i|v\rangle\langle v|H_{el}|f\rangle}{E_f-E_v}. \qquad (3)$$

The initial, intermediate, and final states in Eqs. (2) and (3) are described by wave functions of the type |photon; exciton; phonon⟩. For the sake of simplicity, we shall first assume that the temperature is $T=0$ and that only spontaneous creation of phonons occurs; all the necessary phonon factors will be given in the final expressions. Then, in the ground state $|0\rangle$ there is a photon with a momentum $\mathbf{q}$ and a polarization $\mathbf{e}$, i.e., $|0\rangle=|\mathbf{q},\ \mathbf{e};\ 0;\ 0\rangle$; in the intermediate state $|v\rangle$ there is a direct exciton with a momentum $\mathbf{k}$ and an energy $E_v=E_\beta(\mathbf{k})$, i.e., $|v\rangle=|0;\ \mathbf{k},\ \beta;\ 0\rangle$. The final state $|f\rangle$ corresponds to an indirect exciton with a quasimomentum $\mathbf{K}_s$ and an energy $\varepsilon_\alpha^s(\mathbf{K}_s)$, and a phonon of the σ branch with a momentum $\varkappa_m$ and an energy $\hbar\Omega\varkappa_s$, i.e., $|f\rangle=|0;\mathbf{K}_s,\ \alpha,s;\ \varkappa_s,\ \sigma\rangle$ (the index s labels the conduction band valleys).

In the relationship (3), the quantity $\mathbf{j}$ is the current operator and H_{el} is the Hamiltonian of the electron-phonon interaction. Out of all the possible virtual states $|v\rangle$, we shall consider only those which correspond to the minimum value of the energy denominator in Eq. (3), i.e., we shall consider transition from the upper valence band to the nearest conduction band. The quasimomenta of an indirect exciton $\mathbf{K}_s$ and of a phonon $\varkappa_s$ will be measured from the point $\mathbf{K}_{0s}$, which is at the bottom of the valley corresponding to the absolute minimum of the conduction band.

In the case of sufficiently weak Coulomb interaction the matrix elements of Eq. (3) can be regarded as independent of the small momenta $\mathbf{K}_s$ and $\varkappa_s$ (Ref. 3). In fact, if the Coulomb interaction is weak, the exciton states originate from the hole and electron states near the extrema of the corresponding energy band and the phonons participating in the interaction with excitons correspond to a limited region of the Brillouin zone near the point $\mathbf{K}_{0s}$. The energy denominator E_f-E_v on the right-hand side of Eq. (3) may be replaced by a constant if the virtual state is not too close (compared with the exciton binding energy) to the final state. Then, the intermediate states correspond to free electron-hole pairs. The wave functions describing the virtual state are products of the basis wave functions of the valence and conduction bands:

$$|0,\beta\rangle=|0,v\rangle|0,c\rangle,$$
$$|\mathbf{K}_{0s},\beta\rangle=|\mathbf{K}_{0s},v\rangle|\mathbf{K}_{0s},c\rangle. \qquad (4)$$

The matrix elements of Eq. (3) differ from zero for $\mathbf{K}_s+\varkappa_s-\mathbf{q}=0$ and are proportional to the probability of finding an electron and a hole at the same point in space.[3] The wave function of an indirect exciton for $\mathbf{r}_e=\mathbf{r}_h$ and $\mathbf{K}_s=0$ is a product of an envelope function $F_\alpha(0)$, describ-

 0038-5646/85/080313-04$04.00

ing the relative motion of an electron and a hole, and of Bloch functions which correspond to the valence and conduction bands, modulate the envelope function, and are taken at the critical points $\mathbf{k}_h = 0$ and $\mathbf{k}_e = \mathbf{K}_{0s}$ (Ref. 4). Therefore, a matrix element described by Eq. (3) can be represented approximately by

$$\langle 0|M^i(\mathbf{q})|f\rangle = F_\alpha(0)\left[\frac{1}{\Delta E_c}\langle 0|e^{i\mathbf{q}\mathbf{r}}j^i|0,\beta\rangle\langle 0,\beta|H_{el}|\alpha,s\rangle + \frac{1}{\Delta E_v}\langle 0|e^{i\mathbf{q}\mathbf{r}}j^i|\mathbf{K}_{0s},\beta\rangle\langle \mathbf{K}_{0s},\beta|H_{el}|\alpha,s\rangle\right]. \quad (5)$$

The quantities ΔE_c and ΔE_v are given by the expressions

$$\Delta E_c = E_c(0) - E_c(\mathbf{K}_{0s}), \quad \Delta E_v = E_v(0) - E_v(\mathbf{K}_{0s}). \quad (6)$$

An explicit calculation of the quantities in Eq. (5) requires knowledge of the specific electron-phonon interaction Hamiltonian H_{el}. Following Refs. 5 and 6, we shall confine ourselves to symmetry considerations, which allow us to reduce the matrix elements to a certain number of constants and also to determine the dependence of each matrix element on the quantities $\mathbf{K}_{0s}$, $\mathbf{e}$, and σ.

We shall assume that the conduction band minima are located in the momentum space along the [100] axes. A typical example is Si. The fundamental absorption of Si corresponds to indirect exciton transitions between the top of the valence band Γ_8^+ (or Γ_{25}' without allowance for the spin) and six Δ minima of the conduction band.[7] Transitions assisted by all kinds of phonons are allowed.[8] We shall consider the strongest transition assisted by a transverse optical phonon. Symmetry properties of an indirect exciton are governed by the group C_{4v}. In view of the anisotropy of the conduction band, the lowest exciton state is split at $\mathbf{K}_s = 0$ into two quadruply degenerate levels, one of which correspond to light holes and the other to heavy holes. The basis wave functions of the ground state are

$$|\alpha, s\rangle = |\gamma, \eta; s\rangle = \Psi_\gamma^s \varphi_s \eta. \quad (7)$$

The functions Ψ_γ^s are the basis wave functions of holes in the $|\mathbf{J}, m_J\rangle_s$ representation (the valley index $s = x, y, z$ labels the quantization axis); the spatial part of the electron wave function φ_s transforms in accordance with the Δ_1 representation of the C_{4v} group; $\eta = \{\alpha_e \beta_e\}$ represents spin functions. Selecting the quantization axis along the z axis, we find that[5]

$$\begin{aligned}
\Psi_1^z &= |{}^3/_2, {}^3/_2\rangle_z = 2^{-1/2}(yz+ixz)\alpha_h,\\
\Psi_2^z &= |{}^3/_2, {}^1/_2\rangle_z = 6^{-1/2}[2xy\alpha_h - (yz+ixz)\beta_h],\\
\Psi_3^z &= |{}^3/_2, -{}^1/_2\rangle_z = 6^{-1/2}[2xy\beta_h - (yz-ixz)\alpha_h],\\
\Psi_4^z &= |{}^3/_2, -{}^3/_2\rangle_z = 2^{-1/2}(yz-ixz)\beta_h.
\end{aligned} \quad (8)$$

The functions Ψ with the upper indices x and y can be obtained from the system (8) by cyclic transposition of x, y, and z. The number of nonzero linearly independent components of the matrix element is (see, for example, Ref. 4)

$$N_0 = \frac{1}{h}\sum_g \chi_\mu^*(g)\chi_\nu(g)\chi_\varkappa(g), \quad (9)$$

where χ_μ, χ_ν and $\chi_\varkappa$ are the characters of the corresponding representations; h is the order of the group; the summation in Eq. (9) is carried out over all the elements of the group g. It should be noted that the electron-photon interaction operator $\mathbf{j}$ transforms in accordance with the representation Γ_{15}, whereas the wave functions of the virtual state $|k_{0s}, \beta\rangle$ transform in accordance with Δ_5; the representation corresponding to the state $|0, \beta\rangle$ is reducible:

$$\Gamma_{25}' \times \Gamma_{15} = \Gamma_{15} + \Gamma_{25} + \Gamma_{12}' + \Gamma_2'. \quad (10)$$

It is easily shown that in the dipole approximation for the matrix elements $\langle 0|j^i|0,\beta\rangle$ and $\langle 0|j^i|\mathbf{K}_{0s},\beta\rangle$, we obtain $N_0 = 1$ for the virtual states Γ_{15} and Δ_5, whereas $N_0 = 0$ applies to the other states. Bearing in mind that the operator H_{el} for the *TO* phonons transforms in accordance with the representation Δ_5, we find that the matrix elements $\langle 0, c|H_{el}|\mathbf{K}_{0s}, c\rangle$ and $\langle 0, v|H_{el}|\mathbf{K}_{0s}, v\rangle$ also have one nonzero independent component each. Therefore, the matrix element $\langle 0|M^i(0)|f\rangle$ reduces to two quantities: W_T (for the virtual state Γ_{15}) and Q_T (for Δ_5):

$$\langle 0|M^i(0)|f\rangle = W_T f_{\gamma\eta}^{is\sigma} + Q_T g_{\gamma\eta}^{is\sigma}. \quad (11)$$

Here, f and g are the numerical functions, and the index σ represents the transverse phonon polarization.

When the contributions of all the nonresonant terms are included in the background permittivity, the tensor ε in the vicinity of the ground state of an indirect exciton is finally obtained in the form

$$\varepsilon_{ij}(\omega, \mathbf{q}) = \varepsilon_{ij}^{(0)}(\omega) - \frac{4\pi}{\omega^2 V}\mathscr{P} \times \sum_{\mathbf{K}_s,\gamma,s} |F_\gamma(0)|^2 \frac{D_{\gamma s}^{ij}}{\hbar\omega - \varepsilon_\gamma^s(\mathbf{K}_s) - \hbar\Omega_{\mathbf{K}_{0s}-\mathbf{q}}}, \quad (12)$$

where the symbol $\mathscr{P}$ in front of the sum indicates that the summation over the quasimomentum K_s applies to the principal value;

$$D_{\gamma s}^{ij} = \sum_{\eta,\sigma} (W_T f_{\gamma\eta}^{is\sigma} + Q_T g_{\gamma\eta}^{is\sigma})(W_T f_{\gamma\eta}^{js\sigma} + Q_T g_{\gamma\eta}^{js\sigma})^*. \quad (13)$$

The numerical functions f and g are calculated in accordance with Eqs. (5) and (11) allowing for the definitions (7) and (8). If $i \neq j$, all the quantities D vanish. The values of D are listed in Table I for the case when $i = j$. We recall that the index i represents the direction of polarization of light $\mathbf{e}$: if $i = x, y, z$, we have, respectively, $\mathbf{e}$ [100], [010], [001]

If $\mathbf{q} \ll \mathbf{K}_{0s}$, the phonon energy $\hbar\Omega_{\mathbf{K}_{0s}-\mathbf{q}}$ can be expanded as a series in the vicinity of the point $\mathbf{K}_{0s}$. For example, in the case of the zth valley, we have

$$\hbar\Omega_{\mathbf{K}_{0z}-\mathbf{q}} \approx \hbar\Omega_{\mathbf{K}_{0z}} + A\mathbf{n}\mathbf{q} + B_\parallel q_z^2 + B_\perp(q_x^2 + q_y^2), \quad (14)$$

where $n = \{0, 0, 1\}$ is a unit vector in the direction of $\mathbf{K}_{0z}$.

We shall consider only the case of parabolic dispersion of the exciton energy band and assume that

$$\varepsilon_\gamma^s(\mathbf{K}_s) = E_g - R_\gamma + (\hbar^2 K_s^2/2M_\parallel + \hbar^2 K_\perp^2/2M_\perp), \quad (15)$$

where $M_\parallel$, K_s and $M_\perp$, $K_\perp$ are the longitudinal and transverse values of the mass and phonon momentum. We shall

TABLE I

ν	$s=x$			$s=y$			$s=z$		
	$e\parallel[001]$	$e\parallel[100]$	$e\parallel[010]$	$e\parallel[001]$	$e\parallel[100]$	$e\parallel[010]$	$e\parallel[001]$	$e\parallel[100]$	$e\parallel[010]$
$\lvert 3/2, 3/2\rangle$	0	W_T^2	0	0	0	W_T^2	W_T^2	0	0
$\lvert 3/2, -3/2\rangle$	0	W_T^2	0	0	0	W_T^2	W_T^2	0	0
$\lvert 3/2, 1/2\rangle$	$2/3R_T^2$	$1/3W_T^2$	$2/3R_T^2$	$2/3R_T^2$	$2/3R_T^2$	$1/3W_T^2$	$1/3W_T^2$	$2/3R_T^2$	$2/3R_T^2$
$\lvert 3/2, -1/2\rangle$	$2/3R_T^2$	$1/3W_T^2$	$2/3R_T^2$	$2/3R_T^2$	$2/3R_T^2$	$1/3W_T^2$	$1/3W_T^2$	$2/3R_T^2$	$2/3R_T^2$

Note: The following notation is used in the above table:
$W_T = (\sqrt{2}\Delta E_c)^{-1}\langle\Gamma_{25}'|j|\Gamma_{15}\rangle\langle\Gamma_{15}|H_{el}|\Delta_1\rangle$, $Q_T = (\sqrt{2}\Delta E_v)^{-1}\langle\Gamma_{25}'|H_{el}|\Delta_5\rangle\langle\Delta_5|j|\Delta_1\rangle$,
$R_T = W_T + Q_T$.

also ignore the splitting Δ of the ground state of an indirect exciton ($\Delta \sim 0.3$ meV is quoted in Ref. 9 for Si) and bear in mind that in experimental studies of the transmission of light the energy deficit is $\delta \gg \Delta$.

Then, substituting the values from Table I and the expansion (14) in Eqs. (12) and (1), and also writing down explicitly the phonon factors, we find that the summation over the quasimomentum $\mathbf{K}_s$ and over the valleys s gives the following expression in the first nonvanishing approximation in respect of the wave vector:

$$\Delta\varepsilon(\omega,\mathbf{q}) = -\frac{2^{3/2}M_\parallel^{1/2}M_\perp q^2}{\hbar^2\omega^2} D_T\left\{ n_T(\mathbf{K}_0)\left[\frac{A^2}{2\delta_+^{3/2}} - \frac{B_\parallel - B_\perp}{\delta_+^{1/2}}\right] + [n_T(\mathbf{K}_0)+1]\left[\frac{A^2}{2\delta_-^{3/2}} + \frac{B_\parallel - B_\perp}{\delta_-^{1/2}}\right]\right\}. \quad (16)$$

Here the functions $n_T(\mathbf{K}_0)$ are the phonon occupation numbers,

$$D_T = W_T^2|F_1(0)|^2 + {}^1/_3(W_T^2 - 2R_T^2)|F_2(0)|^2, \quad (17)$$

$$\delta_\mp = E_g - R \pm \hbar\Omega_{\mathbf{K}_0} - \hbar\omega. \quad (18)$$

The formula (16) is valid at frequencies ω such that

$$\delta_\mp \gg \hbar\Omega_{\mathbf{K}_0} q/K_0. \quad (19)$$

Similar calculations can be carried out also in the case of Ge. We shall confine ourselves to a listing of the main differences from the preceding case and give the final results. The minima of the conduction band of Ge are located in the momentum space at the point L at the edge of the Brillouin zone. The basis wave functions of the exciton states transform in accordance with representations of the group D_{3d} and represent a superposition of states described by Eq. (7). Since the bottom of a valley corresponds to the edge of the Brillouin zone, the constant A in the expression for the phonon energy (14) vanishes.

According to the experimental data,[5] the element Ge is characterized by $\Delta E_v \gg \Delta E_c$ and, consequently, the transitions assisted by phonons in the valence band can be ignored. When phonons are scattered by electrons, both longitudinal acoustic and transverse optical phonons take part.[8] We shall consider only the LA phonon because it is stronger. The corresponding operator of the electron-phonon interaction H_{el} transforms in accordance with the L_2' representation.[8] Consequently, the value of $\Delta\varepsilon$ is given by the following expression valid at optical frequencies governed by the inequality (19):

$$\Delta\varepsilon(\omega,\mathbf{q}) = \frac{2^{1/2}M_\parallel^{1/2}M_\perp q^2}{9\hbar^2\omega^2} D_L(B_\perp - B_\parallel) \times\left[\frac{n_L(\mathbf{K}_0)+1}{\delta_-^{1/2}} - \frac{n_L(\mathbf{K}_0)}{\delta_+^{1/2}}\right], \quad (20)$$

where

$$D_L = W_L^2[|F_1(0)|^2 + {}^1/_3|F_2(0)|^2]. \quad (21)$$

It follows from Eqs. (16) and (20) that the birefringence of cubic crystals in the region of indirect exciton transitions is due to the anisotropy of the matrix element and of the phonon spectrum. The polarization dependence of the matrix elements is a consequence of the many-valley structure of the conduction band. Therefore, the nonsphericity of the conduction band at the point $\mathbf{k} = 0$ is the cause of the optical anisotropy of cubic crystals. Since the phonon constants A and B are of the order of the ratios $\hbar\Omega_{\mathbf{K}_0}$ and $\hbar\Omega_{k0}/K_0^2$ respectively, the birefringence is governed not only by the spatial dispersion parameter $(qa)^2$, but also by the ratio of the phonon energy $\hbar\Omega_{\mathbf{K}_0}$ to the deficit $\delta_\mp$. In the region of indirect exciton transitions is quite realistic to expect a small energy deficit when the ratio $\hbar\Omega_{\mathbf{K}_0}/\delta_\pm$ becomes of the order of unity or larger. Since in the optical part of the spectrum we have $(aq)^2 \sim 10^{-6}$, it follows that the birefringence is $\Delta\varepsilon(\omega,\mathbf{q})/n_0^2 \sim 10^{-6}$–$10^{-5}$. According to Eqs. (16) and (20), the effect rises resonantly on approach to an exciton absorption line.

The author is grateful to L. V. Keldysh for his interest, to I. B. Levinson for valuable discussions and halpful comments, and also to Yu. N. Berozashvili for an opportunity to see some unpublished experimental results that have stimulated the present investigation.

[1]V. M. Agranovich and V. L. Ginzburg, Kristallooptika s uchetom prostranstvennoĭ dispersii i teoriya éksitonov, Nauka, M., 1979 (Crystal Optics with Spatial Dispersion and Excitons, 2nd ed., Springer Verlag, Berlin, 1984).
[2]E. G. Tsitsishvili, Fiz. Tekh. Poluprovodn. **15**, 1983 (1981); [Sov. Phys. Semicond. **15**, 1152 (1981)]; O. V. Gogolin, E. G. Tsitsishvili, J. L. Deiss, C. Klingshirn, and V. E. Solomko, Pis'ma Zh. Eksp. Teor. Fiz. **34**, 328 (1981) [JETP Lett. **34**, 312 (1981)].
[3]R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
[4]G. L. Bir and G. E. Pikus, Simmetriya i deformatsionnye effekty v poluprovodnikakh, Nauka, M., 1972 (Symmetry and Strain-Induced Effects in Semiconductors, Wiley, New York, 1975).
[5]D. L. Smith and T. C. McGill, Phys. Rev. *B* **14**, 2448 (1976).
[6]V. M. Asnin, G. L. Bir, Yu. N. Lomasov, G. E. Pikus, and A. A. Roga-

chev, Zh. Eksp. Teor. Fiz. **71**, 1600 (1976) [Sov. Phys. JETP **44**, 838 (1976)]; G. E. Pikus, Fiz. Tverd. Tela (Leningrad) **19**, 1653 (1977) [Sov. Phys. Solid State **19**, 965 (1977)]; V. D. Kulakovskiĭ, G. E. Pikus, and V. B. Timofeev, Usp. Fiz. Nauk **135**, 237 (1981) [Sov. Phys. Usp. **24**, 815 (1981)].
[7]G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. B **111**, 1245 (1958).
[8]M. Lax and J. J. Hopfield, Phys. Rev. **124**, 115 (1961).
[9]J. -C. Merle, M. Capizzi, P. Fiorini, and A. Frova, Phys. Rev. B **17**, 4821 (1978).

Translated by A. Tybulewicz