

## Chapter 2

# Exciton Paramagnetic, Paraelectric, and Zero-Field Resonances

The Coulomb binding of electrons and holes into excitons causes peculiarities in their resonance absorption of the energy of a microwave electromagnetic field. In addition to information about the structure of the conduction and valence bands, obtained by means of spin resonance of the conduction electrons (holes), exciton paramagnetic resonance can yield information about the exciton energy spectrum. The possible existence of paramagnetic resonance on excitons in semiconductors was noticed by Deigen and Pekar [70], but after their pioneer work no successful investigations were carried out for a long time, either theoretically or experimentally.<sup>1</sup>

In a low-density exciton gas ( $n_{\text{ex}}a_{\text{ex}} \ll 1$ ), which is what we consider in this chapter, the width of the exciton paramagnetic resonance line cannot be influenced by the exciton–exciton interaction. During the exciton–exciton collisions, processes with reciprocal spin reorientation of interrelating excitons are possible, affected, in particular, by the exchange electron scattering of one exciton on the hole of another one due to the mechanism of long-range Coulomb interactions (annihilation interaction of an electron and a hole of different excitons). However, for a low exciton concentration the contribution of this mechanism is lower compared with the contribution to the value of transverse exciton spin relaxation from dephasing, with the reorientation of exciton spins during their intraband spin-dependent scattering on phonons. In undoped crystals longitudinal exciton spin relaxation is also determined by the interaction of spin excitons with phonons.

Here and further the concept of the spin exciton is not used in a literal sense. In the model of simple energy bands, as was mentioned in Sect. 1.1, the exciton states can be split into para states and ortho states. In all other cases the projection of the total angular momentum of the electron and hole in the exciton is not a good quantum number. In this case it turns out that if we build a Hamiltonian of the interaction of the localized magnetic moment (or the external magnetic field) with

---

<sup>1</sup>We are talking about direct detection of the paramagnetic resonance of excitons. Indirect (optical) detection of exciton paramagnetic resonance, which has been realized experimentally in the crystal GaSe, will be discussed in Chap. 5.



the excitons in terms of exciton operators of creation and destruction (see Chap. 4), then we can see from this Hamiltonian that the turnover of the spins of the paramagnetic centers leads to transitions between different exciton bands with a change in both the quantum numbers of relative electron–hole motion and the exciton wave vector. An external alternating magnetic field of the respective polarization causes similar transitions. On this basis, in those cases when the exciton states are not characterized by a definite spin projection, we shall conditionally apply the concept of exciton spin and, respectively, the concept about the processes of the exciton spin–lattice relaxation if magnetic dipole transitions are possible between the exciton states.

The utilization of the method of correlation functions and graphic techniques of Konstantinov–Perel' [275] (which was used for a study of electron paramagnetic resonance (EPR) line shape by Aminov [276]) allows us to consider different mechanisms of exciton spin–lattice relaxation. Because the valence bands of most semiconductors are built from the  $p$  and  $d$  states (in rare-earth semiconductors from the  $f$  states) which correspond to different-from-zero values of the orbital angular momenta of the valence electrons, the modulation of spin–orbital interaction by lattice vibrations in the valence band causes the effective mechanism of the exciton spin–lattice relaxation.

This chapter discusses the contribution to the exciton spin–lattice relaxation of the dynamic contact hyperfine interaction between electron components of the free excitons ( $s$  electrons of the conduction band, which are coupled with the holes from the valence band during the formation of free excitons) with the nuclear spins in the nodes of the crystalline lattice, although the low efficiency of this relaxation mechanism is pre-evident. What is interesting here is the fact that, despite the complete averaging of the hyperfine interaction during the motion of the individual exciton [70], for the system of excitons there exists a different-from-zero contribution to the linewidth of the exciton paramagnetic resonance due to the hyperfine interaction of all electrons and holes coupled in excitons with the crystal nuclei.

With regard to paraelectric resonance, despite the case of localized paraelectric centers or the so-called “noncentral ions” having the ability to tunnel between some equilibrium positions, making inhibited but not translational movements, in the case of excitons the electric dipole moments are translated through the crystal. Paraelectric resonance of excitons, despite sufficient evidence of its existence, has previously not been considered at all either in molecular crystals or in semiconductors. An interesting feature of paraelectric resonance of excitons in semiconductors is the lack of the isotopic shift effect of the paraelectric resonance lines for the intraserial exciton transitions and the presence of a large isotopic shift of the lines of interserial paraelectric resonance.

Finally, this chapter suggests and theoretically justifies the idea of using a large set of initial splittings of exciton levels in crystalline fields of different semiconductors to generate coherent electromagnetic radiation in the submillimeter and far-infrared (IR) ranges at intra- and interserial exciton transitions and also to generate coherent magnons by excitons in magnetic semiconductors.

The main results of this chapter are published in [170, 277–282].



## 2.1 Paramagnetic Resonance of Small-Radius Triplet Excitons

We shall consider the features of the paramagnetic resonance spectra of small-radius excitons using the example of triplet excitons in organic crystals containing aromatic molecules such as naphthalene [283]. The aromatic molecules in the triplet state are characterized by initial spin level splitting. Removal of the triple spin degeneration may be complete or partial, depending on the symmetry of the molecule and the nature of the molecular wave function of the triplet state. In aromatic molecules, the initial splitting of spin levels is conditioned by the dipole–dipole interaction between electron spins

$$\mathcal{H}_D = g_e^2 \mu_B^2 \sum_{i < j} [(\mathbf{S}_i \mathbf{S}_j) r_{ij}^{-3} - 3(\mathbf{r}_{ij} \mathbf{S}_i)(\mathbf{r}_{ij} \mathbf{S}_j) r_{ij}^{-5}], \quad (2.1)$$

where the sum is taken over all electrons of the molecule,  $g_e$  is the electron  $g$ -factor,  $\mu_B$  is Bohr's magneton,  $\mathbf{S}_i$  is the spin operator of the  $i$ th electron, and  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ , where  $\mathbf{r}$  is the electron coordinate.

After averaging operator  $\mathcal{H}_D$  on the coordinate part of the wave function, we may represent it as

$$\mathcal{H}_D = D \left( S_z^2 - \frac{1}{3} \mathbf{S}^2 \right) + E (S_x^2 - S_y^2), \quad (2.2)$$

where  $D$  and  $E$  are constants of the spin Hamiltonian.

Since the energy of the spin–spin interaction is often compared in magnitude to the Zeeman energy corresponding to the operator

$$\mathcal{H}_z = -g_e \mu_B \sum_i \mathbf{S}_i \mathbf{H}$$

(for naphthalene, for example,  $D = 0.1006 \text{ cm}^{-1}$  and  $E = 0.0138 \text{ cm}^{-1}$ ), the EPR spectra are highly anisotropic. In particular, the anisotropic EPR spectrum of a naphthalene solid solution in durene contains four lines. Each pair of lines is caused by two differently orientated locations of the naphthalene molecules in durene (naphthalene and durene crystals belong to the monoclinic system and have two molecules in the elementary cell). Four lines merge into two at certain orientations of the external magnetic field (as evidenced by the elements of crystal symmetry).

The EPR spectrum of the lowest triplet excited state in pure aromatic single crystals is qualitatively different from the EPR spectrum of the excited triplet states of the molecules from which the crystal is built. This difference is particularly important if (1) there are two or more molecules in the elementary cell that are not connected by the inversion center, and (2) the Davydov splitting of the triplet state is greater than the  $D$  and  $E$  constants. Thus, for example, the paramagnetic resonance spectrum of the triplet excitons in naphthalene consists of two lines due to dipole–dipole interaction (2.1) for any orientations of the external magnetic field.



Also, since the triplet exciton is spread over many molecules, the hyperfine structure of the EPR spectra, as has already been indicated, is washed away due to the protons, in contrast to the proton hyperfine structure observed at isolated molecules.

The EPR spectrum from two lines does not necessarily indicate the existence of coherent exciton waves. When the wave of excitation undergoes strong scattering by lattice vibrations, then the propagation of this excitation may be regarded as a random process or as diffusion. If in addition  $\tau^{-1} \gg |D|, |E|$ , then the EPR spectrum is averaged on all nonequivalent positions of molecules in the elementary cell. Here  $\tau$  is the characteristic time of the disordered movement between two neighbors in the elementary cell that is not transferred from one to the other at translation.

Singlet and triplet excitons in the molecular crystals at low levels of optical excitation and without their interaction with the lattice vibrations can be considered on the basis of elementary perturbation theory. If  $|s\rangle$  is the wave function of the crystal in which the molecule  $s$  is in the first excited state, but all other  $N - 1$  molecules ( $N$  is the number of molecules in the crystal) are in the ground state, then the energy of the singlet excitons is the solutions of the  $N \times N$  secular determinant

$$|\langle s | \mathcal{H}_0 | s' \rangle - \langle s | s' \rangle E| = 0, \quad (2.3)$$

where  $\mathcal{H}_0$  contains the kinetic and Coulomb electron energy. If  $|t\rangle$  is the lowest triplet exciton state, then all the matrix elements of the type  $\langle t | \mathcal{H}_0 | t' \rangle$  in (2.3) are reduced to two-electron exchange integrals (containing the orbitals of different molecules) that are small. For the triplet excitons the effects of the intermolecular charge transfer can contribute to the width of the absorption bands. Taking into account these effects, it is necessary to replace  $\mathcal{H}_0$  by

$$\mathcal{H}_1 = \mathcal{H}_0 + \sum_{t, t'} R_{tt'} |t\rangle \langle t'|,$$

where

$$R_{tt'} = \sum_{\mathbf{K}} (E_{\mathbf{K}m} - E_0)^{-1} \langle \mathbf{K}, m | \mathcal{H}_0 | t' \rangle \langle \mathbf{K}, m | \mathcal{H}_0 | t \rangle.$$

Here,  $|\mathbf{K}, m\rangle$  is the ionized state taking into consideration the intermolecular charge transfer ( $\mathbf{K}$  is the wave vector and  $m$  is the band index). Then the energies of the triplet excitons are the solutions of the secular determinant

$$|\langle t' | \mathcal{H} | t' \rangle - \langle t | t' \rangle E| = 0. \quad (2.4)$$

Let  $\lambda$  denote the location of the molecule in the  $n$ th elementary cell with the number of elementary cells  $n = 1, 2, 3, \dots$ . Let  $|n\lambda M\rangle$  be the antisymmetric wave function of the crystal in which the molecule  $n\lambda$  is excited in the lowest triplet electron state with the spin projection  $M$  and the rest of the molecules are in the ground state. Then, the wave functions diagonalizing the secular determinant (2.4) have the form [283]

$$|\mathbf{K}\lambda M\rangle = \frac{1}{N} \sum_n |n\lambda M\rangle \exp\{2\pi i \mathbf{kR}_{n\lambda}\},$$



where  $\mathbf{R}_{n\lambda}$  is the coordinate of the molecule  $n\lambda$ . Taking into consideration the nonequivalences of the molecule locations in the elementary cell ( $\lambda \neq \lambda'$ ), the exciton wave functions diagonalizing the determinant (2.4) have the form

$$|\mathbf{K}_l M\rangle = \sum_{\lambda} C_{l\lambda} |\mathbf{K}\lambda M\rangle.$$

Here  $l$  is the index of the triplet exciton band. The relationship between the coefficients  $C_{l\lambda}$  can be found in specific cases on the basis of symmetry properties.

In order to calculate the parameters of the spin Hamiltonian describing the paramagnetic resonance spectrum of the excitons, we shall divide the Brillouin zone into two regions  $P$  and  $Q$ , which relate, respectively, to the cases of nondegenerate and degenerate exciton bands. In region  $P$ , for which the wave vectors of the excitons correspond to the nondegenerate exciton bands, without considering the spin we can use a  $3 \times 3$  determinant to find the spin energy levels:

$$|\langle \mathbf{K}_l M | \mathcal{H}_D + \mathcal{H}_Z | \mathbf{K}_l M' \rangle - E \delta_{MM'}| = 0. \quad (2.5)$$

Since the operator  $\mathcal{H}_D + \mathcal{H}_Z$  is invariant under the transformations of the crystal translation group, it is sufficient to consider the matrix elements between states with the same  $\mathbf{K}$ .

In the  $Q$  region, where there is a degeneracy (not considering the spin) of the exciton bands or a quasi-degeneracy (when the distance between bands is of the order of the spin–spin interaction constants), it is necessary to replace (2.5) by

$$|\langle \mathbf{K}_l M | \mathcal{H}_D + \mathcal{H}_Z | \mathbf{K}'_l M' \rangle - E \delta_{MM'} \delta_{ll'}| = 0,$$

where  $l$  is now the number of degenerate (quasi-degenerate) exciton bands.

The excitons with the wave vectors  $\mathbf{K}$  from the  $P$  region of the Brillouin zone have an exciton paramagnetic resonance spectrum that is not dependent on  $\mathbf{K}$ , whereas the paramagnetic resonance spectrum of the excitons with the wave vectors  $\mathbf{K}$  from the  $Q$  region strongly depends on  $\mathbf{K}$ .

The degeneracy of exciton bands can be affected by the symmetry properties or may be accidental. The Hamiltonians  $\mathcal{H}_0$  and  $\mathcal{H}$  are invariant to the symmetry operations of the crystal space group and to the time-reversal transformation. In aromatic crystals the degeneracy of the exciton bands due to time-reversal symmetry has been revealed (benzene may also have an accidental degeneracy) [283].

The matrix element of the spin–spin interaction operator may be presented as follows:

$$\begin{aligned} \langle \mathbf{K}_l M | \mathcal{H}_D | \mathbf{K}_l M' \rangle &= \sum_{\lambda} |C_{l\lambda}|^2 \langle n\lambda M | \mathcal{H}_D | n\lambda M' \rangle \\ &+ \sum_{\lambda} F(\mathbf{K}_l \lambda M M') + \sum_{\lambda < \lambda'} G(\mathbf{K}_l \lambda \lambda' M M'), \end{aligned} \quad (2.6)$$



where

$$F(\mathbf{K}_l \lambda M M') = \sum_{t(t \neq n)} |C_{l\lambda}|^2 \langle n\lambda M | \mathcal{H}_D | t\lambda M' \rangle \exp\{2\pi i \mathbf{K}(\mathbf{R}_{t\lambda} - \mathbf{R}_{n\lambda})\},$$

$$G(\mathbf{K}_l \lambda \lambda' M M') = \sum_t C_{l\lambda}^* C_{l\lambda'} \langle n\lambda M | \mathcal{H}_D | t\lambda' M' \rangle \exp\{2\pi i \mathbf{K}(\mathbf{R}_{t\lambda'} - \mathbf{R}_{n\lambda})\}$$

$$+ C_{l\lambda} C_{l\lambda'}^* \langle t\lambda M | \mathcal{H}_D | n\lambda' M' \rangle \exp\{2\pi i \mathbf{K}(\mathbf{R}_{n\lambda} - \mathbf{R}_{t\lambda'})\}.$$

The numerical estimation for the  $\mathbf{K}$ -dependent terms from (2.6) in the case of naphthalene gives [283]

$$0 < \varepsilon(\mathbf{K}_l, \lambda' M M') < 4.8 \cdot 10^{-4} \text{ cm}^{-1},$$

where

$$\varepsilon(\mathbf{K}_l, \lambda' M M') = \left| \sum_{\lambda} F(\mathbf{K}_l, \lambda M M') - \sum_{\lambda < \lambda'} G(\mathbf{K}_l, \lambda \lambda' M M') \right|.$$

This value is much smaller than the energy of the spin–spin interaction; therefore, the matrix element (2.6) may be represented with a high degree of accuracy as

$$\langle \mathbf{K}_l M | \mathcal{H}_D | \mathbf{K}_l M' \rangle \sim \frac{1}{2} \{ \langle M | \mathcal{H}_S^{(\text{I})} | M' \rangle + \langle M | \mathcal{H}_S^{(\text{II})} | M' \rangle \}. \quad (2.7)$$

Here  $\mathcal{H}_S$  is the spin Hamiltonian of rhombic symmetry determined by (2.2), in which the axes  $x$  and  $y$  correspond to the axis of molecular elongation and compression. The upper indices (I) and (II) of  $\mathcal{H}_S$  in (2.7) represent two nonequivalent positions of the molecule in the elementary cell.

In order to simplify the calculation of the spin energy levels, it is convenient to select the crystal screw axis as a quantization axis. In this coordinate system the spin energy levels obtained by solving the secular equation (2.5) in the case of the naphthalene crystal are the eigenvalues of the spin Hamiltonian

$$\mathcal{H}_S = -0.00588 \left( S_z^2 - \frac{1}{3} \mathbf{S}^2 \right) - 0.00345 (S_x^2 - S_y^2)$$

$$+ 0.0332 (S_x S_y + S_y S_x),$$

where the energy is expressed in  $\text{cm}^{-1}$ .

In this way one can obtain the spin Hamiltonians for the triplet excitons in any molecular crystal.

## 2.2 Spin-Dependent Intraband Scattering of Triplet Wannier–Mott Excitons on Phonons

The experimental technique used for the excitation of semiconductors by optical means or by an electron beam has reached the level necessary to create a concentra-



tion of excitons that allows the observation of the resonance paramagnetic absorption effect of microwaves by excitons. The value of the necessary exciton concentration was estimated in the work [70]. According to this estimation, the stationary concentration of excitons created in the crystal during optical band–band transitions is determined by the formula

$$n_{\text{ex}} = \tau_{\text{ex}} \Phi \kappa / \hbar \omega, \quad (2.8)$$

if we assume that exciton de-excitation occurs only due to the processes of radiative recombination, that is, if nonradiative de-excitation processes of excitons are not important. Here  $\Phi$  is the light flow per unit of illuminated area and per unit of time,  $\kappa$  is the coefficient of the exciton absorption of light in the crystal,  $\omega$  is the frequency of the absorbed light, and  $\tau_{\text{ex}}$  is the average lifetime of the exciton (at  $\Phi = 1 \text{ W/cm}^2$ ,  $\kappa \sim 10^5$ ,  $\hbar \omega \sim 1 \text{ eV}$ , and  $\tau_{\text{ex}} \sim 10^{-8} \text{ s}$ ,<sup>2</sup> according to (2.8) we obtain  $n_{\text{ex}} \simeq 10^{16} \text{ cm}^{-3}$ ).

Electron spin resonance on excitons is discussed in [70]. In this process a microwave quantum is actually absorbed by the electron with reorientation of its spin. After absorbing microwave quanta the excitons have a longer lifetime with respect to luminescence than ordinary excitons, as the projection of the electron spin is changed with the electron spin resonance, and the total spin of the excited crystal becomes different from zero, unlike the zero spin of the crystal in the ground state. This apparently corresponds to the case when the Zeeman energy is much greater than the energy of exchange splitting of the exciton. Another case proposed for consideration in the work [284] is the absorption of the energy of a microwave magnetic field at the transitions between the Zeeman components of the energy spectrum of the triplet exciton.

Spin–lattice relaxation of excitons, as already mentioned in this chapter, is determined by different mechanisms of interaction of the electrons and holes (coupled into excitons) with phonons. As explained at the beginning of this chapter, we shall consider the modulation by lattice vibrations of the contact hyperfine interaction of the electrons coupled into excitons with the magnetic moments in the nodes of the crystal lattice.

Another reason for this consideration is that hyperfine interaction, on one hand, is in a number of cases a dominant factor determining the width of the EPR line (local electron and hole centers in alkali halide crystals), and, on the other hand, it does not contribute to the linewidth of the single free exciton in the same crystals.

The Hamiltonian of the contact hyperfine interaction between the spins of intrinsic electrons of the crystal and the nuclear spins in the presence of an external constant magnetic field has the form (it is assumed that hyperfine splitting is much

---

<sup>2</sup>At low temperatures ( $k_0 T < \text{Ry}^{\text{ex}}$ ) in sufficiently pure semiconductors, it was established according to extensive experimental data that the lifetime of direct excitons actually has a value on the order taken in [70] ( $10^{-9} \text{ s} \leq \tau_{\text{ex}} \leq 10^{-7} \text{ s}$  [97]).



less than Zeeman splitting) [14]

$$\mathcal{H}_{IS} = \frac{8\pi}{3} \gamma_e \gamma_N \hbar^2 \sum_i \sum_n S_{zi} I_{zn} \delta(\mathbf{r}_i - \mathbf{R}_n), \quad (2.9)$$

where  $\gamma_e$  and  $\gamma_N$  are the gyromagnetic ratios for the electron and nucleus,  $\mathbf{r}_i$  and  $\mathbf{R}_n$  are radius vectors of the  $i$ th electron and the  $n$ th nucleus, respectively (it is assumed that all the magnetic nuclei in the crystal are the same), and  $S_{zi}$  and  $I_{zn}$  are the spin projection operators of the  $i$ th electron and the  $n$ th nucleus. We shall pass in (2.9) to the representation of the second quantization, taking into account that in the node representation the state of a single electron in a crystal is described by a set of quantum numbers  $\mathbf{f}, \lambda, \sigma$ :

$$\begin{aligned} \mathcal{H}_{IS} = & \frac{8\pi}{3} \gamma_e \gamma_N \hbar^2 \sum_n \sum_{\mathbf{f}, \mathbf{f}'} \sum_{\lambda, \lambda'} \psi_{\lambda}^*(\mathbf{R}_n - \mathbf{f}) \psi_{\lambda'}(\mathbf{R}_n - \mathbf{f}') \\ & \times (a_{\mathbf{f}\lambda\uparrow}^+ a_{\mathbf{f}'\lambda'\uparrow} - a_{\mathbf{f}\lambda\downarrow}^+ a_{\mathbf{f}'\lambda'\downarrow}) I_{zn}. \end{aligned} \quad (2.10)$$

Here  $\psi_{\lambda}(\mathbf{R}_n - \mathbf{f})$  is the wave function of the electron in an atom that is situated in a crystal node  $\mathbf{R}_n$ ,  $\mathbf{f}$  is the vector defining the electron position relative to its intrinsic nucleus,  $\lambda$  is the discrete quantum number characterizing the non-spin electron state,  $\sigma$  is the spin projection ( $\sigma = \downarrow, \uparrow$ ), and  $a_{\mathbf{f}\lambda\sigma}^+$  and  $a_{\mathbf{f}\lambda\sigma}$  are the operators of creation and destruction of the electron in the  $|\mathbf{f}\lambda\sigma\rangle$  state.

In the future we will discuss the electron scattering process on the phonons in the presence of contact hyperfine interaction but without changing the spin projections of the nuclei. Therefore, deriving the Hamiltonian of the interaction of electron spins with phonons from which the Hamiltonian of the spin-dependent intraband scattering of excitons on the phonons can be obtained, we shall replace the operator  $\mathbf{I}_z$  by its eigenvalue  $M_I$ .

In order to account for the modulation effects of the hyperfine interaction by lattice vibrations, we shall represent the radius vector of the  $n$ th nucleus in the form  $\mathbf{R}_n = \mathbf{R}_n^0 + \mathbf{U}_n$ , where  $\mathbf{R}_n^0$  determines the nucleus equilibrium position in the  $n$ th lattice node, and  $\mathbf{U}_n$  is the displacement vector of the nucleus from this position due to thermal vibrations. Let us expand the operator (2.10) in a series according to the shift of the nuclei from their equilibrium positions (limited to linear terms) and express  $\mathbf{U}_n$  in terms of normal coordinates of the crystal  $q_{\mathbf{x}\alpha}$  ( $\mathbf{x}$  is the wave vector,  $\alpha$  is the branch of vibrations) taking into account the cyclical conditions. Then we obtain the Hamiltonian of the spin-dependent interaction of electrons with vibrations of atoms in nodes of the crystalline lattice.

In the continuum approximation that we use, the electron interacts only with the longitudinal acoustic vibrations:

$$(\mathbf{e}_{\mathbf{x}_l}, \mathbf{x}_l) = x_l, \quad (\mathbf{e}_{\mathbf{x}_t}, \mathbf{x}_t) = 0, \quad (2.11)$$

where  $\mathbf{x}_l(\mathbf{x}_t)$  and  $\mathbf{e}_{\mathbf{x}_l}(\mathbf{e}_{\mathbf{x}_t})$  are the wave vector and the unit vector of polarization for longitudinal (transversal) acoustic vibrations, respectively.



Let us pass from the normal coordinates of the crystal  $\mathbf{q}_{\mathbf{r}_l}$  to the phonon creation and destruction operators  $B_{\mathbf{r}_l}^+$  and  $B_{\mathbf{r}_l}$  and, also, from the electron operators  $a_{\mathbf{r}_{\lambda\sigma}}^+$  and  $a_{\mathbf{r}_{\lambda\sigma}}$  to the exciton operators  $A_{\mathbf{K}M_S}^+$  and  $A_{\mathbf{K}M_S}$  ( $\mathbf{K}$  and  $M_S$  are the wave vector and the spin projection of the triplet exciton) by means of orthonormalized wave functions of the orthoexciton recorded in the node representation:

$$\begin{aligned}\psi_{\mathbf{K}\nu,1} &= \frac{1}{\sqrt{N}} \sum_{\mathbf{g},\mathbf{h}} e^{i(\mathbf{K},\alpha\mathbf{g}+\beta\mathbf{h})} \varphi_{\nu}(\mathbf{g}-\mathbf{h}) a_{\mathbf{g}\uparrow}^+ b_{\mathbf{h}\uparrow}^+ |0\rangle, \\ \psi_{\mathbf{K}\nu,0} &= \frac{1}{\sqrt{2N}} \sum_{\mathbf{g},\mathbf{h}} e^{i(\mathbf{K},\alpha\mathbf{g}+\beta\mathbf{h})} \varphi_{\nu}(\mathbf{g}-\mathbf{h}) (a_{\mathbf{g}\uparrow}^+ b_{\mathbf{h}\downarrow}^+ + a_{\mathbf{g}\downarrow}^+ b_{\mathbf{h}\uparrow}^+) |0\rangle, \\ \psi_{\mathbf{K}\nu,-1} &= \frac{1}{\sqrt{N}} \sum_{\mathbf{g},\mathbf{h}} e^{i(\mathbf{K},\alpha\mathbf{g}+\beta\mathbf{h})} \varphi_{\nu}(\mathbf{g}-\mathbf{h}) a_{\mathbf{g}\downarrow}^+ b_{\mathbf{h}\downarrow}^+ |0\rangle,\end{aligned}\quad (2.12)$$

where  $|0\rangle$  is the wave function of the vacuum state, the sum is taken over the lattice nodes,  $\varphi_{\nu}(\mathbf{g}-\mathbf{h})$  is the hydrogen-like wave function describing the relative motion of the electron and hole in the exciton ( $\nu$  is a set of quantum numbers characterizing the state of the relative motion),  $e^{i(\mathbf{K},\alpha\mathbf{g}+\beta\mathbf{h})}$  is the translational part of the wave function ( $\alpha$  and  $\beta$  are the ratios of the effective masses of the electrons and holes to the exciton mass), and  $a_{\mathbf{g}\sigma}^+$  and  $b_{\mathbf{h}\sigma'}$  are the creation operators of the electron and hole with the spin projections  $\sigma$  and  $\sigma'$  in the corresponding lattice nodes  $\mathbf{g}$  and  $\mathbf{h}$ .

Note that the spin indices of the operators  $a_{\mathbf{g}\sigma}^+$  and  $b_{\mathbf{h}\sigma'}$  from (2.12) correspond to two different spinor bases,<sup>3</sup> belonging to different quasi-particles (electrons and holes). Thus, the spin operators of the holes  $S_z^h, S_{\pm}^h = S_x^h \pm iS_y^h$  differ from the corresponding electron spin operators  $S_z^e, S_{\pm}^e$  only by replacing operators  $a^+$ ,  $a$  by  $b^+$ ,  $b$ :

$$\begin{aligned}S_z^{(p)} &= \frac{1}{2} \sum_{\mathbf{f}\lambda} (\alpha_{\mathbf{f}\lambda\uparrow}^+ \alpha_{\mathbf{f}\lambda\uparrow} - \alpha_{\mathbf{f}\lambda\downarrow}^+ \alpha_{\mathbf{f}\lambda\downarrow}), \\ S_+^{(p)} &= \sum_{\mathbf{f}\lambda} \alpha_{\mathbf{f}\lambda\uparrow}^+ \alpha_{\mathbf{f}\lambda\downarrow}, \\ S_-^{(p)} &= \sum_{\mathbf{f}\lambda} \alpha_{\mathbf{f}\lambda\downarrow}^+ \alpha_{\mathbf{f}\lambda\uparrow},\end{aligned}\quad (2.13)$$

where

$$\alpha_{\mathbf{f}\lambda\sigma}^{(p)} (\alpha_{\mathbf{f}\lambda\sigma}^{+(p)}) = \begin{cases} a_{\mathbf{f}\lambda\sigma} (a_{\mathbf{f}\lambda\sigma}^+), & p = e, \\ b_{\mathbf{f}\lambda\sigma} (b_{\mathbf{f}\lambda\sigma}^+), & p = h. \end{cases}\quad (2.14)$$

It can be seen that the wave functions (2.12) are indeed the eigenfunctions of the operators  $S_z^e + S_z^h$  and  $(\mathbf{S}_e + \mathbf{S}_h)^2$ , built on the basis of the operators (2.13),

<sup>3</sup>For the simple energy bands of the free carriers that we consider in this section, these bases coincide accurately to the designations.



(2.14). Therefore, the use of these spin operators and their corresponding wave functions (2.12) seems more convenient in comparison with the case when the complex-conjugated electron spinor basis is applied to characterize the spin part of the wave function of the hole from the exciton. In this latter case, for example, the paraexciton and orthoexciton with zero spin projection are characterized by symmetric and, respectively, antisymmetric spin wave functions with respect to transposition of the spin variables [98, 166, 168]. In contrast, the wave functions (2.12) correspond to the usual rules of addition of the angular momenta of the electrons and holes (whose operators are given in natural spinor bases), the singlet state, as usual, being antisymmetric, and the triplet one being symmetric with respect to the permutations of the electron and hole spin coordinates.

The spin operators of the holes from (2.13) (the case  $p = h$ ) are obtained by taking into account the transition rules for the hole creation and destruction operators according to Bir and Pikus [44]:

$$b_{\mathbf{f}\lambda\sigma}^+ = a_{\hat{\mathcal{K}}(\mathbf{f}\lambda\sigma)}, \quad b_{\mathbf{f}\lambda\sigma} = a_{\hat{\mathcal{K}}(\mathbf{f}\lambda\sigma)}^+,$$

where  $\hat{\mathcal{K}}$  is the time-reversal operator.

After the introduction of exciton creation and destruction operators  $A_{\mathbf{K}M_S}^+$  and  $A_{\mathbf{K}M_S}$ , the Hamiltonian of the spin-dependent interaction of triplet excitons with phonons, describing the intraband exciton–phonon scattering, will take the form

$$\begin{aligned} \mathcal{H}_1 = & \frac{1}{\sqrt{N}} \sum_{\mathbf{K}, \mathbf{K}'} \theta(\mathbf{K}, \mathbf{K}'; S, I) (A_{\mathbf{K},1}^+ A_{\mathbf{K}',1} - A_{\mathbf{K},-1}^+ A_{\mathbf{K}',-1}) \\ & \times (B_{\mathbf{K}-\mathbf{K}'} + B_{\mathbf{K}'-\mathbf{K}}^+), \end{aligned} \quad (2.15)$$

where  $N$  is the number of atoms in the crystal, and  $B_{\mathbf{K}'-\mathbf{K}}^+$  and  $B_{\mathbf{K}-\mathbf{K}'}$  are the creation and destruction operators of the longitudinal acoustic phonons with wave vectors  $\mathbf{q} = \mathbf{K}' - \mathbf{K}$  and  $-\mathbf{q}$ , respectively.

The constant of the spin-dependent exciton–phonon interaction  $\theta(\mathbf{K}, \mathbf{K}'; S, I)$  in (2.15) is determined by the formula

$$\begin{aligned} \theta(\mathbf{K}, \mathbf{K}'; S, I) = & -\frac{\sqrt{2}\pi}{3} \cdot \frac{M_I \mu_B \mu_N}{IS\gamma_0} \sqrt{\frac{\hbar|\mathbf{K}-\mathbf{K}'|}{m_a v_l}} \frac{1}{\sqrt{N}} \sum_{\mathbf{g}\mathbf{g}'\mathbf{h}} \varphi_{1S}^*(\mathbf{g}-\mathbf{h}) \varphi_{1S}(\mathbf{g}'-\mathbf{h}) \\ & \times \exp\{-i\alpha\mathbf{K}\mathbf{g} + i\alpha\mathbf{K}'\mathbf{g}' + i\beta(\mathbf{K}'-\mathbf{K})\mathbf{h}\} \\ & \times [(1+i)\mathcal{I}_1 + (1-i)\mathcal{I}_2], \end{aligned} \quad (2.16)$$

where

$$\begin{aligned} \mathcal{I}_1 = & \int d^3R \psi_{2S}^*(\mathbf{R}-\mathbf{g}) \psi_{2S}(\mathbf{R}-\mathbf{g}') \exp\{i(\mathbf{K}-\mathbf{K}')\mathbf{R}\}, \\ \mathcal{I}_2 = & \int d^3R \psi_{2S}^*(\mathbf{R}-\mathbf{g}) \psi_{2S}(\mathbf{R}-\mathbf{g}') \exp\{i(\mathbf{K}'-\mathbf{K})\mathbf{R}\}. \end{aligned}$$



In (2.16)  $m_a$  is the mass of the atom,  $v_l$  is the speed of the longitudinal acoustic phonons, and  $\mathcal{V}_0$  is the volume of the elementary cell. The summation over  $\mathbf{g}$ ,  $\mathbf{g}'$ , and  $\mathbf{h}$  in (2.16) is performed on all lattice nodes. Here, for simplicity, we consider a model of a crystal for which the ground state corresponds to the hydrogen-like wave functions of  $1s$ -type valence electrons, which, after optical excitation by  $\pi$ -polarized light, are transferred into a  $2s$ -type state with the formation of  $\Gamma_6 \otimes \Gamma_6 \otimes \Gamma_1$ -excitons.

Following the normalization conditions for the wave functions of the orthoexciton (2.12), the functions of relative motion of the electron-hole in the exciton  $\varphi_{1S}(\mathbf{g} - \mathbf{h})$  and  $\varphi_{1S}(\mathbf{g}' - \mathbf{h})$  from (2.16) are normalized to the volume of the elementary cell of the crystal  $\mathcal{V}_0$ .

According to (2.16), at  $\mathbf{K} = \mathbf{K}'$  the constant of spin-dependent exciton-phonon interaction  $\theta(\mathbf{K}, \mathbf{K}', S, I)$  becomes zero. It can be shown that the absence of bonding between long-wave phonons ( $\boldsymbol{\kappa}_l = \mathbf{K} - \mathbf{K}' \rightarrow 0$ ) and the spins of the conduction electrons, holes, or triplet excitons is a general property of such spin-phonon interactions, regardless of the concrete mechanism of phonon bonding with the spins of the specified elementary excitations.

## 2.3 Contribution of Hyperfine Interaction to Exciton Paramagnetic Resonance Linewidth

The contribution of the exciton-phonon spin-dependent interaction to the linewidth of the exciton paramagnetic resonance may be estimated using the correlation functions method or on the basis of the graphical techniques of Konstantinov and Perel' [275] developed for paramagnetic resonance by Aminov [276, 285]. The general scheme of the spin-lattice relaxation by these methods (we shall use the first of them) is applied to any system regardless of the specific types of relaxation transitions.<sup>4</sup> Therefore, before finalizing the explicit form of the operator  $\mathcal{H}_1$  of exciton-phonon interaction, we can use the formulas of this section to describe the exciton-phonon relaxation without using an explicit form of the bonding constant  $\theta(\mathbf{K}, \mathbf{K}', S, I)$  from (2.16). In particular, the contact hyperfine exciton interaction and the exciton exchange interaction with the paramagnetic centers can be treated in a unified way.

We shall present the Hamiltonian of the exciton-phonon system in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \quad (2.17)$$

where

$$\mathcal{H}_0 = \sum_{\mathbf{K}, M_S} E_{M_S}(\mathbf{K}) A_{\mathbf{K}, M_S}^+ A_{\mathbf{K}, M_S} + \sum_{\boldsymbol{\kappa}_\alpha} \hbar \omega_{\boldsymbol{\kappa}_\alpha} B_{\boldsymbol{\kappa}_\alpha}^+ B_{\boldsymbol{\kappa}_\alpha} \quad (2.18)$$

---

<sup>4</sup>This is true if we are interested in the behavior of a system for not very small time scales after the switching of the external excitation when the details of its initial state have already become nonessential [286].



is the Hamiltonian of the free excitons and phonons, and the operator  $\mathcal{H}_1$  was determined above (formula (2.15)). Further, we shall introduce the  $\mathcal{H}_t$  operator for the interaction of triplet excitons with the alternative magnetic field. The  $x$ -component of the magnetic moment of triplet excitons is determined by

$$\begin{aligned} \mathcal{M}_x^{\text{ex}} = & \frac{1}{2\sqrt{2}}\mu_B(g_h - g_e) \sum_{\mathbf{K}} (A_{\mathbf{K},1}^+ A_{\mathbf{K},0} + A_{\mathbf{K},0}^+ A_{\mathbf{K},1} \\ & + A_{\mathbf{K},-1}^+ A_{\mathbf{K},0} + A_{\mathbf{K},0}^+ A_{\mathbf{K},-1}), \end{aligned} \quad (2.19)$$

where  $\mu_B$  is the Bohr magneton, and  $g_e$  and  $g_h$  are the effective  $g$ -factors of the electron and hole. Then for linear polarization of the microwave field, the operator  $\mathcal{H}_t$  has the form

$$\mathcal{H}_t = -2\mathcal{M}_x^{\text{ex}} H_1 e^{\varepsilon t} \cos \omega t,$$

where the operator  $\mathcal{M}_x^{\text{ex}}$  is determined by the formula (2.19),  $H_1$  is the amplitude of the magnetic component of the microwave, and  $\varepsilon$  is the adiabatic parameter of the connection of the electromagnetic field of frequency  $\omega$ .

The  $\mathcal{H}_t$  operator causes quantum transitions between the orthoexciton states, from which we shall select the two lowest states  $\Psi_{\mathbf{K},-1}(n=1, l=0, M_s=-1)$  and  $\Psi_{\mathbf{K},0}(n=1, l=0, M_s=0)$  for consideration. The total transition probability per time unit between these states summed on the final states and averaged on the initial ones (for the given value of the exciton wave vector  $\mathbf{K}$ ) is

$$\begin{aligned} P(\mathbf{K}, \omega) = & \frac{(g_e - g_h)^2}{32\hbar^2} (\mu_B H_1)^2 \int_{-\infty}^{\infty} dt e^{i\omega t} \\ & \times \langle A_{\mathbf{K},-1}^+(t) A_{\mathbf{K},0}(t) A_{\mathbf{K},0}^+(0) A_{\mathbf{K},-1}(0) \rangle_{\mathcal{H}}. \end{aligned} \quad (2.20)$$

Here the statistical averaging is performed by means of the Hamiltonian  $\mathcal{H}$  from (2.17);  $A_{\mathbf{K},-1}^+(t)$  and  $A_{\mathbf{K},0}(t)$  are the operators of creation and destruction of excitons with the wave vector  $\mathbf{K}$  and corresponding to the spin projections  $M_s = -1$  and  $M_s = 0$  in Heisenberg's representation. In deriving (2.20) we used the integral representation of Dirac's  $\delta$ -function.

According to the definition, we shall introduce the following correlation function:

$$F_{\mathbf{K}}(t) = e^{i\omega_0 t} \langle A_{\mathbf{K},-1}^+(t) A_{\mathbf{K},0}(t) A_{\mathbf{K},0}^+(0) A_{\mathbf{K},-1}(0) \rangle_{\mathcal{H}}, \quad (2.21)$$

where  $\hbar\omega_0 = (E_{\mathbf{K},0} - E_{\mathbf{K},-1})$  is the exciton Zeeman splitting. Then for transition probability  $P(\mathbf{K}, \omega)$ , instead of (2.20), we obtain

$$P(\mathbf{K}, \omega) = \frac{(g_e - g_h)^2}{32\hbar^2} (\mu_B H_1)^2 \int_{-\infty}^{\infty} F_{\mathbf{K}}(t) e^{i(\omega - \omega_0)t} dt. \quad (2.22)$$

In formula (2.21) the statistical average for the correlation function  $F_{\mathbf{K}}(t)$

$$\langle \dots \rangle_{\mathcal{H}} = \frac{\langle \mathcal{U}(\beta) \dots \mathcal{H}_0 \rangle}{\langle \mathcal{U}(\beta) \rangle_{\mathcal{H}_0}} \quad (2.23)$$



is performed by means of the evolution operator

$$\mathcal{U}(\beta) = T \exp \left\{ - \int_0^\beta d\lambda \mathcal{H}_1(\lambda_1) \right\},$$

where  $\hat{T}$  is the Dyson time-regulating operator,  $\mathcal{H}_1(\lambda)$  is operator  $\mathcal{H}_1$  in the representation of interaction,  $\beta = (k_0 T)^{-1}$ ,  $k_0$  is Boltzmann's constant, and  $T$  is temperature. The averaging on the right side of (2.23) is performed on the Hamiltonian of zero approximation from (2.18), where the known series from thermodynamic perturbation theory is used for the evolution operator  $\mathcal{U}(\beta)$  [287, 288].

Formula (2.21) is initial during the calculation of the spectral moments of the  $n$ th order of the line of exciton paramagnetic resonance under consideration by  $n$ th differentiating of the correlation function

$$(-i)^n M_n(\mathbf{K}) = \left. \frac{\partial^n}{\partial t^n} F_{\mathbf{K}}(t) \right|_{t=0}. \quad (2.24)$$

By means of formulas (2.24) and (2.21) and the equations of motion for the operators  $A_{\mathbf{q},-1}^+(t)A_{\mathbf{K},0}(t)$ ,  $B_{\mathbf{q}-\mathbf{K}}(t)$  and  $B_{\mathbf{q}-\mathbf{K}}^+(t)$  in the Heisenberg representation we find the following expression for the second moment of the absorption line:

$$\begin{aligned} M_2(\mathbf{K}) = & \frac{1}{\hbar^2 N} \left\{ \sum_{\mathbf{q}\mathbf{q}'} \theta(\mathbf{q}, \mathbf{q}'; S, I) \theta(\mathbf{q}', \mathbf{q}; S, I) \right. \\ & \times \langle A_{\mathbf{q}',-1}^+ A_{\mathbf{K},0} (B_{\mathbf{q}-\mathbf{q}'} + B_{\mathbf{q}-\mathbf{q}'}^+) (B_{\mathbf{q}-\mathbf{K}} + B_{\mathbf{q}-\mathbf{K}}^+) A_{\mathbf{K},0}^+ A_{\mathbf{K},-1} \rangle_{\mathcal{H}} \\ & + \sum_{\mathbf{q}} (T_{\mathbf{K}} - T_{\mathbf{q}} + \hbar\omega_{\mathbf{q}-\mathbf{K}}) \theta(\mathbf{q}, \mathbf{K}; S, I) \\ & \times \langle A_{\mathbf{q},-1}^+ A_{\mathbf{K},0} B_{\mathbf{q}-\mathbf{K}} A_{\mathbf{K},0}^+ A_{\mathbf{K},-1} \rangle_{\mathcal{H}} \\ & + \sum_{\mathbf{q}} (T_{\mathbf{K}} - T_{\mathbf{q}} - \hbar\omega_{\mathbf{K}-\mathbf{q}}) \theta(\mathbf{q}, \mathbf{K}; S, I) \\ & \left. \times \langle A_{\mathbf{q},-1}^+ A_{\mathbf{K},0} B_{\mathbf{K}-\mathbf{q}}^+ A_{\mathbf{K},0}^+ A_{\mathbf{K},-1} \rangle_{\mathcal{H}} \right\}, \quad (2.25) \end{aligned}$$

where  $T_{\mathbf{K}}$  and  $T_{\mathbf{q}}$  are the kinetic energies of excitons with the wave vectors  $\mathbf{K}$  and  $\mathbf{q}$  in the band characterized by the spin projection  $M_S = -1$ , and  $\theta(\mathbf{K}, \mathbf{K}'; S, I)$  is determined by (2.16).

If in the evolution operator  $\mathcal{U}(\beta)$  from (2.3.8a) we are limited by the first item (unit) during its representation in the form

$$\begin{aligned} \mathcal{U}(\beta) = & 1 + \sum_{(n=1)}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\lambda_n \int_0^\beta d\lambda_{n-1} \cdots \int_0^\beta d\lambda_1 \\ & \times \hat{T} \{ \mathcal{H}_1(\lambda_1) \mathcal{H}_1(\lambda_2) \cdots \mathcal{H}_1(\lambda_n) \}, \end{aligned}$$



that corresponds to the averaging in (2.25) by means of the Hamiltonian  $\mathcal{H}_0$ , then for the contribution of the hyperfine interaction to the second moment of the exciton paramagnetic resonance line we obtain

$$M_2(\mathbf{K}) = \frac{1}{\hbar^2 N} \sum_{\mathbf{q}} \theta(\mathbf{q}, \mathbf{K}; S, I) \theta(\mathbf{K}, \mathbf{q}; S, I) n_{\mathbf{K}, -1} \times (n_{\mathbf{K}, 0} + 1)(2m_{\mathbf{K}-\mathbf{q}} + 1), \quad (2.26)$$

where  $n_{\mathbf{K}, M_S}$  and  $m_{\mathbf{K}-\mathbf{q}}$  are, respectively, the average numbers of filling excitons with wave vector  $\mathbf{K}$  and spin projection  $M_S$  and phonons with wave vectors  $\mathbf{K} - \mathbf{q}$ . Note that this formula and the more general equation (2.25) are true only if the energy of the thermal vibrations of the lattice is less than the Zeeman splitting of the exciton, and spin transitions  $0 \rightarrow 1$  in the exciton are not essential compared with transitions  $-1 \rightarrow 0$ .

Formulas (2.26) and (2.25) are applied if the inverted time of the exciton relaxation by the phonons  $\tau_{\text{rel}}^{-1}$  exceeds the transition probability  $P(\mathbf{K}, \omega)$  from (2.22), which in turn must be greater than the inverted time of the exciton life  $\tau_{\text{ex}}^{-1}$  ( $\tau_{\text{ex}}^{-1} < P(\mathbf{K}, \omega) < \tau_{\text{rel}}^{-1}$ ).<sup>5</sup> From formula (2.26) we can see that with decreasing exciton concentration the contribution of hyperfine interaction to the width of the resonance line decreases, and at low exciton occupation numbers it falls practically to zero, in accordance with the results of the work [70] for separate free excitons.

## 2.4 Generation of Coherent Electromagnetic Radiation at Intra- and Interseries Exciton Transitions

The great diversity of optic quantum generators satisfies different scientific and applied purposes to a considerable degree. However, besides the variety of applied optically active media and ways of excitation of the coherent radiation, due to the mastering of submillimeter and far-infrared (far-IR) ranges we come across many difficulties, both in creating sources with a rebuilt frequency of radiation in a wide interval and in selecting the active media for laser generation.

In the far-IR and submillimeter ranges, to create a volumetrical negative differential conduction usually an inverted distribution of the hot carriers of the current in the impulse space is used [289]. The inversion is created due to the accumulation of carriers in a region of closed trajectories [290], where the electron energy is less than the energy of the optical phonon. In particular, in p-Ge crystals in sufficiently strongly crossed electric  $\mathbf{E}$  and magnetic  $\mathbf{H}$  fields there is a superpopulation in the subband of light holes, which is preserved even at comparatively high concentrations of impurities ( $n_{\text{imp}} \sim 5 \cdot 10^{15} \text{ cm}^{-3}$ ) and lattice temperatures from liquid

---

<sup>5</sup>For a more general expression of (2.25) including the case of nonequilibrium thermodynamic states, the first of these inequalities can probably be weakened.



helium to liquid nitrogen temperatures. This causes a negative absorption coefficient of the far-IR radiation [291]. The far-IR radiation is generated at direct optical transitions from the band of light holes in p-Ge to the band of heavy holes under conditions of the inversion of the distribution function of light holes relative to the heavy ones [292]. The creation of an inverted function of the free carrier distribution is possible, not only in external crossed  $\mathbf{E}$  and  $\mathbf{H}$  fields, but also in their absence with the capture of electrons (holes) by shallow impurities in semiconductors [293].

The possibility of resonance parametric generation of submillimeter waves of frequency  $\omega_3 = \omega_2 - \omega_1$  from the region of the lattice absorption at high levels of semiconductor excitation by bichromatic light with  $\omega_1, \omega_2 \gtrsim E_g/\hbar$  ( $E_g$  is the energy gap) is theoretically shown in [294]. This way of generating submillimeter radiation is not convenient, because its realization requires the presence of a quasi-energy spectrum of the “charge carrier + bichromatic electromagnetic field” system, which can exist only in the presence of strong optical pumping.

In this section, in the frame of a two-band model, we consider a mechanism for generating coherent electromagnetic radiation in the microwave and far-IR ranges at resonance transitions between the states of the relative electron–hole movement in Wannier–Mott excitons [277]. The energy spectrum of the excitons is determined by the electrostatic interaction of electrons and holes (Coulomb and exchange contributions), accounting for spin–orbital coupling in the conduction and valence bands, as well as the influence of the crystal field on excitons (the initial splitting of degenerate exciton bands in the crystal field).<sup>6</sup> Since all these values essentially depend on the chemical composition of the crystals, their spatial symmetry, and the constants of the crystal field, there is a great choice of exciton bands for the realization of laser generation in the submillimeter and far-IR regions of the spectrum. Laser generation at transitions between the exciton bands has the characteristic features influenced by the possibility to create an inversion of the exciton band populations by selective coupling of electron–hole pairs into excitons of one (upper) band. It turns out that only a small concentration of excitons in the crystal is necessary to achieve the autoexcitation threshold of this type of laser.

The Hamiltonian of the exciton–photon system for the case of one photon mode and two exciton bands in “the rotating field” approximation (ignoring the antiresonance terms) has the form

$$\begin{aligned}
 H = \hbar\omega C^+ C + \sum_{\mathbf{K}} \varepsilon_n(\mathbf{K}) A_{n\mathbf{K}}^+ A_{n\mathbf{K}} + \sum_{\mathbf{K}} \varepsilon_{n'}(\mathbf{K}) A_{n'\mathbf{K}}^+ A_{n'\mathbf{K}} \\
 + \sum_{\mathbf{K}} [g_{n'n}(0) C A_{n'\mathbf{K}}^+ A_{n\mathbf{K}} + \text{H.c.}], \quad (2.27)
 \end{aligned}$$

where  $C^+$  and  $C$  are the creation and destruction operators of the photon of frequency  $\omega$ ;  $A_{n\mathbf{K}}^+$  and  $A_{n\mathbf{K}}$  are the creation and destruction operators of the exciton

---

<sup>6</sup>In semiconductors containing heavy atoms, one must also consider the relativistic corrections that can bring, for example, in lead halogenides, an essential reconstruction of the band structure [295].



with wave vector  $\mathbf{K}$  in the band with index  $n$ ;  $\varepsilon_n(\mathbf{K})$  is the exciton energy in the band  $n$ ;  $g_{n'n}(0)$  is the constant of the exciton–photon coupling (Fourier transform of the interaction energy of the excitons with the photons at transitions between exciton bands). Here we do not demonstrate the dependence of operators  $C^+$  and  $C$  on the wave vector and polarization of the photon, since in the microwave and IR ranges the dependence of the matrix elements of the transition on the wave vector of the photon may be ignored, and the exciton states should be selected beforehand with features of symmetry which correspond to the dipole-allowed transitions of the given polarization of photons.

The Hamiltonian (2.27) does not contain terms describing the interaction of excitons and photons with a dissipative subsystem and a pumping subsystem to create the inverted population of exciton bands. We shall consider these subsystems phenomenologically.

The equations of motion for operators of photon fields, exciton polarization and the operators of the population difference of the states  $|n\mathbf{K}\rangle$  and  $|n'\mathbf{K}\rangle$  of different bands have the form:

$$\begin{aligned}
 \frac{dC}{dt} &= -(i\omega + \varkappa)C - \frac{i}{\hbar} g_{n'n}^*(0) \sum_{\mathbf{K}} S_-^{n'n}(\mathbf{K}), \\
 \frac{d}{dt} S_-^{n'n}(\mathbf{K}) &= -[i\omega_{n'n}(\mathbf{K}) + \Gamma_{n'n}] S_-^{n'n}(\mathbf{K}) + 2\frac{i}{\hbar} g_{n'n}(0) C S_z^{n'n}(\mathbf{K}), \\
 \frac{d}{dt} S_z^{n'n}(\mathbf{K}) &= \frac{1}{T_1} \left[ \frac{1}{2} d_{n'n}^{(0)}(\mathbf{K}) - S_z^{n'n}(\mathbf{K}) \right] \\
 &\quad + \frac{i}{\hbar} [g_{n'n}^*(0) C^+ S_-^{n'n}(\mathbf{K}) - g_{n'n}(0) C S_+^{n'n}(\mathbf{K})], \\
 \frac{d}{dt} S_+^{n'n}(\mathbf{K}) &= \left( \frac{d}{dt} S_-^{n'n}(\mathbf{K}) \right)^+; \quad \frac{dC^+}{dt} = \left( \frac{dC}{dt} \right)^+,
 \end{aligned} \tag{2.28}$$

where

$$\begin{aligned}
 S_z^{n'n}(\mathbf{K}) &= \frac{1}{2} (A_{n'\mathbf{K}}^+ A_{n\mathbf{K}} - A_{n\mathbf{K}}^+ A_{n'\mathbf{K}}), \quad S_-^{n'n}(\mathbf{K}) = A_{n\mathbf{K}}^+ A_{n'\mathbf{K}}, \\
 S_+^{n'n}(\mathbf{K}) &= A_{n'\mathbf{K}}^+ A_{n\mathbf{K}}; \quad \hbar\omega_{n'n}(\mathbf{K}) = \varepsilon_{n'}(\mathbf{K}) - \varepsilon_n(\mathbf{K}).
 \end{aligned}$$

The phenomenological constants are introduced in (2.28) by analogy with the two-level theory of lasers [296, 297]:  $\varkappa$  is the constant of photon damping in the exciton–photon interaction;  $\Gamma_{n'n} = \frac{1}{2}(\Gamma_n + \Gamma_{n'})$ ,  $\hbar\Gamma_n$ , and  $\hbar\Gamma_{n'}$  are terms for “the washing away” of bands  $n$  and  $n'$  due to the interaction of excitons with the dissipative subsystem (the washing away of the exciton band is considered independent of  $\mathbf{K}$ , or more precisely, as a measure of this washing away we select the value of the constant of exciton damping at interaction with the lattice vibrations in the actual region of the exciton wave vectors, where this interaction is more effective);  $T_1$  is the longitudinal relaxation time of the excitons (the time of establishment of the equilibrium difference of populations of the exciton states  $|n\mathbf{K}\rangle$  and  $|n'\mathbf{K}\rangle$  due to the



longitudinal relaxation of the excitons is not considered to be dependent on  $\mathbf{K}$ );  $d_{n'n}^{(0)}$  is the initial inverted population of exciton bands  $n$  and  $n'$ , which is conditioned by the pumping and all other noncoherent processes in the absence of laser action.

We shall average (2.28) by means of the density matrix of the system and take into account that in the regime of generation the corpuscular nature of the photon field is not practically evidenced:

$$\begin{aligned}\langle C S_z^{n'n}(\mathbf{K}) \rangle &\simeq \langle C \rangle \langle S_z^{n'n}(\mathbf{K}) \rangle, \\ \langle C S_{\pm}^{n'n}(\mathbf{K}) \rangle &\simeq \langle C \rangle \langle S_{\pm}^{n'n}(\mathbf{K}) \rangle.\end{aligned}\quad (2.29)$$

Then, representing  $\langle C \rangle$  from (2.29) in the form

$$\langle C \rangle = \sqrt{N} e^{-i\Omega t}, \quad (2.30)$$

where  $N$  is the number of photons in the mode, after substituting (2.30) in  $\frac{d}{dt} S_{+}^{n'n}(\mathbf{K})$  of (2.28), for the stationary case we obtain

$$\langle S_{+}^{n'n}(\mathbf{K}) \rangle = -\frac{1}{\hbar} d_{n'n}^{(0)}(\mathbf{K}) g_{n'n}^*(0) \sqrt{N} e^{i\Omega t} [\Omega - \omega_{n'n}(\mathbf{K}) - i\Gamma_{n'n}]^{-1}. \quad (2.31)$$

Substituting (2.31) in  $\frac{d}{dt} S_z^{n'n}(\mathbf{K})$  of (2.28) we have

$$\begin{aligned}\langle S_z^{n'n}(\mathbf{K}) \rangle &= 2d_{n'n}^{(0)}(\mathbf{K}) \left\{ 1 - 4\Gamma_{n'n} T_1 |g_{n'n}(0)|^2 N \right. \\ &\quad \left. \times \frac{1}{\hbar^2} [(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2]^{-1} \right\}.\end{aligned}\quad (2.32)$$

After substituting (2.32) in  $\frac{d}{dt} S_{-}^{n'n}(\mathbf{K})$  of (2.28) we obtain

$$\begin{aligned}\langle S_{-}^{n'n}(\mathbf{K}) \rangle &= -\frac{1}{\hbar} d_{n'n}^{(0)}(\mathbf{K}) g_{n'n}(0) \sqrt{N} \left\{ 1 - 4\Gamma_{n'n} T_1 |g_{n'n}(0)|^2 N \right. \\ &\quad \left. \times \frac{1}{\hbar^2} [(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2]^{-1} \right\} [\Omega - \omega_{n'n}(\mathbf{K}) + i\Gamma_{n'n}]^{-1} e^{-i\Omega t}.\end{aligned}\quad (2.33)$$

From (2.33) we have

$$\begin{aligned}\frac{d}{dt} \langle C^+ \rangle &= (i\omega - \varkappa) \langle C^+ \rangle - \frac{i}{\hbar^2} |g_{n'n}(0)|^2 N \sum_{\mathbf{K}} \frac{d_{n'n}^{(0)}(\mathbf{K})}{\Omega - \omega_{n'n}(\mathbf{K}) - i\Gamma_{n'n}} \\ &\quad \times \left\{ 1 - \frac{4}{\hbar^2} \Gamma_{n'n} T_1 |g_{n'n}(0)|^2 N [(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2]^{-1} \right\} e^{i\Omega t}.\end{aligned}$$



Again using the substitution (2.30), and after the necessary transformations, we obtain

$$\begin{aligned} \varkappa + i(\Omega - \omega) = & \frac{i}{\hbar^2} |g_{n'n(0)}|^2 \sum_{\mathbf{K}} \frac{d_{n'n}^{(0)}(\mathbf{K})}{\Omega - \omega_{n'n}(\mathbf{K}) - i\Gamma_{n'n}} \\ & \times \left\{ -1 + \frac{4}{\hbar^2} \Gamma_{n'n} T_1 |g_{n'n(0)}|^2 N [(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2]^{-1} \right\}. \end{aligned} \quad (2.34)$$

We choose the real and the imaginary parts in (2.34):

$$2\varkappa = \mathcal{G}_1 - \mathcal{G}_2 N, \quad (2.35)$$

where

$$\begin{aligned} \mathcal{G}_1 = & \frac{2}{\hbar^2} \Gamma_{n'n} |g_{n'n(0)}|^2 \sum_{\mathbf{K}} \frac{d_{n'n}^{(0)}(\mathbf{K})}{(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2}, \\ \mathcal{G}_2 = & \frac{8}{\hbar^4} \Gamma_{n'n}^2 T_1 |g_{n'n(0)}|^4 \sum_{\mathbf{K}} \frac{d_{n'n}^{(0)}(\mathbf{K})}{[(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2]^2}. \end{aligned} \quad (2.36)$$

Let us multiply both sides of (2.35) by  $N$ . Then the first term on the right-hand side will describe the increase of the number of photons due to the induced radiation of the photons by the excitons with the given inverted populations. The sum  $\mathcal{G}_2 N$  accounts for the fact that in the process of the laser action the inversion of populations decreases (the effect of “hole burning” in the amplification curve).

From the imaginary part of (2.34) we obtain

$$\Omega - \omega = (\Delta\Omega)_1 + N(\Delta\Omega)_2, \quad (2.37)$$

where

$$\begin{aligned} (\Delta\Omega)_1 = & -\frac{1}{\hbar^2} |g_{n'n(0)}|^2 \sum_{\mathbf{K}} \frac{d_{n'n}^{(0)}(\mathbf{K})(\Omega - \omega_{n'n}(\mathbf{K}))}{(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2}, \\ (\Delta\Omega)_2 = & \frac{4}{\hbar^4} \Gamma_{n'n} T_1 |g_{n'n(0)}|^4 \sum_{\mathbf{K}} \frac{d_{n'n}^{(0)}(\mathbf{K})(\Omega - \omega_{n'n}(\mathbf{K}))}{[(\Omega - \omega_{n'n}(\mathbf{K}))^2 + \Gamma_{n'n}^2]^2}. \end{aligned} \quad (2.38)$$

The indices 1 and 2 in  $\mathcal{G}$  and  $\Delta\Omega$  designate, respectively, the absence and presence of saturation.

From (2.35) (taking into account that  $\mathcal{G}_2 > 0$ ) we find the condition of the autoexcitation of the IR laser (the generation threshold)

$$\mathcal{G}_1 \geq 2\varkappa. \quad (2.39)$$



An analysis of (2.37) and (2.38) shows that the term of the sum  $(\Delta\Omega)_1$  describes the displacement of the frequency of generation conditioned by the prolonged influence of the active substance. This shift is directed to the center of the contour of the amplification and is proportional to the intensity of the pumping. The term of the sum  $N(\Delta\Omega)_2$ , which is proportional to the power of the generation, describes the effect of “the repulsion of downfalls.” The shift of the frequency of generation takes place to the side of the center of the radiation line. This result, along with the consequences from (2.35) about the increased number of photons from the induced radiation and the effect of “hole burning” in the amplification curve, is similar to the results for the two-level theory of lasers [296, 297].

As we can see from (2.35)–(2.39), the shift of the frequency of the line of induced radiation and the generation threshold of the IR laser are determined by the value of the inversion of exciton band populations  $d_{n'n}^{(0)}(\mathbf{K})$ . An evident form  $d_{n'n}^{(0)}(\mathbf{K})$  depends on the method of pumping and the function of the distribution of the excitons in the bands. For an equilibrium distribution of excitons in the bands during the optical pumping, we have

$$d_{n'n}^{(0)}(\mathbf{K}) = \frac{8}{\mathcal{V}}(\pi\alpha)^{3/2}(N_{n'} - N_n)e^{-\alpha\mathbf{K}^2}, \quad (2.40)$$

where  $\alpha = \hbar^2/2m_{\text{ex}}k_0T$ ,  $m_{\text{ex}}$  is the translational effective mass of the exciton, and  $N_n$  and  $N_{n'}$  are, respectively, the full number of excitons in bands  $n$  and  $n'$ ;  $\mathcal{V}$  is the volume of the crystal. Here  $T$  is the temperature of the crystal at “moderate” levels of optical excitation, when the frequency of exciton–phonon collisions is higher than the frequency of interexciton collisions. If the level of excitation is so high that collisions between excitons take place more often than collisions with phonons, then the exciton dipole–dipole reservoir (EDDR) can be separated. In this case  $T$  designates the temperature of the EDDR under the condition that the deviation from equilibrium is not big and a quasi-equilibrium distribution of excitons in the bands is realized.

**Intraserial Exciton Transitions** If bands  $n$  and  $n'$  belong to one exciton series, then for an equilibrium or quasi-equilibrium distribution of excitons in the bands, expressions (2.35) and (2.37) are transformed into the forms

$$\varkappa = F(\Omega)[1 + \Phi(\Omega)], \quad (2.41)$$

$$\Omega - \omega = F(\Omega)[\Phi(\Omega) - 1](\Omega - \omega_{n'n}^{(0)})[(\Omega - \omega_{n'n}^{(0)})^2 + \Gamma_{n'n}^2]^{-1}, \quad (2.42)$$

where

$$F(\Omega) = \Gamma_{n'n}(N_{n'} - N_n)\Lambda(\Omega),$$

$$\Phi(\Omega) = 4\Gamma_{n'n}T_1N\Lambda(\Omega),$$

$$\Lambda(\Omega) = \frac{1}{\hbar^2}|g_{n'n}(0)|^2[(\Omega - \omega_{n'n}^{(0)})^2 + \Gamma_{n'n}^2].$$



Here  $\hbar\omega_{n'n}$  is the energetic distance between the “parallel” exciton bands  $n$  and  $n'$  (the translational exciton masses in both bands are similar).

According to (2.39) and (2.41), during the intraserial exciton transitions the generation threshold of the far-IR laser is determined by the condition

$$N_{n'} - N_n \geq \frac{\varkappa\hbar^2}{\Gamma_{n'n}} \cdot \frac{(\Omega - \omega_{n'n}^{(0)})^2 + \Gamma_{n'n}^2}{|g_{n'n}(0)|^2}. \quad (2.43)$$

As shown from (2.41) and (2.42), due to the intraserial transitions the kinetic energy of the excitons does not influence the conditions of the far-IR laser generation. The threshold of the generation and the shift of the line of the induced radiation depend on the temperature only by means of the phenomenological parameter  $\Gamma_{n'n}$ .

**Interserial Exciton Transitions** In the case of interserial exciton transitions, we have

$$\omega_{n'n}(\mathbf{K}) = \omega_{n'n}^{(0)} + \frac{\hbar(m_{\text{ex}} - m'_{\text{ex}})}{2m_{\text{ex}}m'_{\text{ex}}} \mathbf{K}^2, \quad (2.44)$$

which leads to the additional dependence of the far-IR laser generation on the temperature, conditioned by the difference of the kinetic energy of the excitons in different bands ( $m'_{\text{ex}}$  is the translational mass of the excitons in the band  $n'$ ). In this case (2.35)–(2.38) are not calculated precisely, but they may be found approximately. In particular, at low temperatures when the kinetic energy of the exciton satisfies the condition

$$\frac{\hbar^2 K^2}{2m} < \frac{m'_{\text{ex}}}{m_{\text{ex}} - m'_{\text{ex}}} \hbar(\Omega - \omega_{n'n}^{(0)}),$$

for the generation threshold we obtain

$$N_{n'} - N_n \geq \frac{\varkappa}{\Gamma_{n'n}} \cdot \frac{[\hbar(\Omega - \omega_{n'n}^{(0)}) - \frac{m_{\text{ex}} - m'_{\text{ex}}}{m'_{\text{ex}}} k_0 T]^2 + \hbar^2 \Gamma_{n'n}^2}{|g_{n'n}(0)|^2}.$$

The depth of the downfall in the amplification curve conditioned by the downfall of the inverse populations in the process of the laser action as determined by the expression  $\mathcal{G}_2 N$ , also depends upon the temperature.

The additional temperature dependence due to interserial exciton transitions, from (2.37), (2.38), (2.40), and (2.44), is characteristic for the shift of the frequency of generation to the center of the contour of amplification and the effect of “the repulsion of downfalls.”

We shall evaluate the effect of the IR-laser radiation by exciton gas. In the sums (2.36) and (2.38) the main contribution is given by the terms of the sum in which  $\omega_{n'n}(\mathbf{K}) \sim \Omega$ , but  $\omega_{n'n}(\mathbf{K}) \sim \omega$ ; thus we can approximately replace  $\Omega$  by  $\omega$  in the sums. Because of the exciton–photon interaction, the shift of  $\Omega - \omega_{n'n}^{(0)}$  of the line of radiation near the threshold of the laser generation is less than the contribution to the width of the line from the interaction of the excitons with the dissipative system ( $\Omega - \omega_{n'n}^{(0)} < \Gamma_{n'n}$ ). Thus, after the calculation of the value of constants of



the exciton–photon interaction from (2.43), we obtain the following expression for the condition of self-excitation of the IR laser due to interserial exciton transitions:

$$N_{n'} - N_n \geq \frac{\hbar^3 \omega_{\mathbf{Q}} \varepsilon_{\mathbf{Q}} \Gamma_{n'n} \kappa \mathcal{V}}{2\pi e^2 (E_{n'} - E_n)^2 |\langle n' | \mathbf{e}_{\mathbf{Q}j} \hat{\mathbf{r}} | n \rangle|^2} \Big|_{Q \rightarrow 0}, \quad (2.45)$$

where  $\omega_{\mathbf{Q}}$  is the frequency of the photon with wave vector  $\mathbf{Q}$  and unit vector of polarization  $\mathbf{e}_{\mathbf{Q}j}$ ,  $\varepsilon_{\mathbf{Q}}$  is the dielectric constant on the frequency  $\omega_{\mathbf{Q}}$ , conditioned by all the excitations of the crystal without the given exciton, and  $\hat{\mathbf{r}}$  is the operator of the coordinate that characterises the electron–hole relative movement in the exciton.

For the transition  $2P_0 \rightarrow 1S$ , from (2.45) we find that

$$N_{2P_0} - N_{1S} \geq 0.9 \frac{\hbar^3 \omega_{\mathbf{Q}} \varepsilon_{\mathbf{Q}} \Gamma_{2P_0,1S} \kappa \mathcal{V}}{\pi (ea_{\text{ex}})^2 (E_{2P_0} - E_{1S})^2}, \quad (2.46)$$

where  $a_{\text{ex}}$  is the exciton Bohr radius.

According to (2.46), for the crystal CdS ( $\mathcal{V} = 10^{-5} \text{ cm}^3$ ,  $\varepsilon_{\mathbf{Q}} = 9.27$ ,  $a_{\text{ex}} = 28.7 \text{ \AA}$  [170],  $\hbar\omega_{\mathbf{Q}} \simeq E_{2P_0} - E_{1S} = 19 \text{ meV}$  [86],  $\kappa\Gamma_{2P_0,1S} \sim 10^{18} \text{ s}^{-2}$  [97, 298]), the threshold of the laser generation at the transition  $2P_0 \rightarrow 1S$  is achieved at  $n_{2P_0}^{\text{ex}} - n_{1S}^{\text{ex}} \gtrsim 0.75 \cdot 10^{10} \text{ cm}^{-3}$ . In the conditions of the inversion of populations at relatively low exciton concentration in the crystal CdS ( $n_{\text{ex}} \sim 10^{14} \text{ cm}^{-3}$ ), the laser generation at the transition  $2P_0 \rightarrow 1S$  begins as soon as the ratio of the exciton concentrations from different bands becomes different from 1 and this difference is not less than  $10^{-4}$ .

## 2.5 Generation of Coherent Magnons in Magnetic Semiconductors

Coherent collective excitations in crystals have attracted attention because of their possible practical use based on their high frequency and phase stabilities. Akhiezer et al. [50] were the first to indicate the possibility of creating coherent magnons in 1963. Due to the interaction of spin waves with the drifting charge carriers, a binding between the spin and the drifting waves takes place, when their frequencies coincide. This binding and, along with it, the amplification of the spin waves can also occur when the frequencies of the spin and drifting waves are not in resonance [299]. To achieve this, it is sufficient to apply an external constant electric field, which helps to change the drifting speed of the electron. Then, if the drifting speed of the free carriers exceeds the phase speed of the spin wave, the spin wave is amplified. This mechanism of spin wave amplification is similar to the mechanism of acoustic wave amplification in piezo-semiconductors [300]. In the limiting case of the absence of collisions between electrons, the coefficient of absorption of the spin waves is equal to zero, and their absorption or amplification is not possible.

In the classical description of spin wave amplification, the length of the spin wave is considered to be much bigger than the length of the free run of the electron  $l$  ( $kl < 1$ ,  $k$  is the wave number of the spin wave), and its frequency is less



than the frequency of the electron collisions. The amplification of spin waves in a ferromagnetic semiconductor is studied in [301] with electron–magnon interaction in the quantum mechanical limit (case  $kl > 1$ ), and it is shown that spin wave amplification takes place, as in the classical case, if the drifting speed of the charge carriers exceeds the phase speed of the spin waves. Another spin wave amplification method is that of parametric excitation of the spin waves with a given value of the wave vector [52].

We shall consider the method of generation and amplification of the coherent magnons in magnetic semiconductors with their optical excitation in the exciton region of the spectrum. A characteristic peculiarity of magnetic semiconductors is the presence of a strong  $s - d(f)$  exchange interaction of the free carriers with localized magnetic moments, which greatly determines the energetic structure of these crystals in the magnetic ordered phase [17]. We note that, in contrast to the “magnetic” excitons of small radius, for whose formation the state of the carriers from the narrow energy bands is important [302], the Wannier–Mott excitons that we consider are formed during the Coulomb coupling of the holes from the valence band with the electrons from the conduction band, the width of which is much greater than the energy of the exchange interaction between free and localized electrons ( $W \gg JSM(T)/M(0)$ ;  $J$  is the exchange integral,  $S$  is the spin of the localized atom with the unbuild  $d(f)$ -shell in the node of the crystal lattice,  $M(0)$  is the magnetization of saturation at  $T = 0$ ). If the value of the exchange splitting of the conduction band is much bigger than the splitting of the valence band (e.g., as in  $\text{CdCr}_2\text{Se}_4$  and  $\text{EuO}$  [303]), then below the phase transition point the exciton spectrum consists of two series: one corresponds to the bound states of the electron from the low spin-polarized conduction subband and the hole of the valence band; the other corresponds to the bound states of the electron from the upper spin-polarized conduction subband and the hole from the valence band.

Strictly speaking, it is necessary to introduce “correct” magnons [304] in the spin wave region for a correct description of the interaction of magnons with the free carriers. Thus, one should consider the contribution of the spins of the electron and hole coupled into an exciton to oscillations of the total angular momentum of the system. With  $T \gg T_o$  ( $T_o$  is the characteristic temperature depending on the  $s - d(f)$  exchange interaction,  $d(f) - d(f)$  interionic exchange interaction, effective mass of carriers and lattice constant [304]) the spin polaron in ferromagnetic semiconductors with wide band dissociate in the temperature interval  $T_o \ll T \ll T_c$  ( $T_c$  is the Curie temperature), the exciton–magnon interaction can be considered without taking into account the “correct” magnons.

Exciton–magnon interaction will be considered here in the frame of the approach developed in Sect. 2.4 for the interaction of excitons with low-frequency electromagnetic radiation. Now the difference is that, in the equations of motion, we shall preserve the dependence on the wave vector of the magnon, which could be ignored for photons.

In the “rotating field” approximation, the Hamiltonian of the interaction between excitons and magnons in the model of two exciton bands and one magnon mode has



the form [278]

$$\begin{aligned}
 H = & \hbar\omega_{\mathbf{q}} B_{\mathbf{q}}^+ B_{\mathbf{q}} + \sum_{\mathbf{K}} \varepsilon_{\sigma}(\mathbf{K}) A_{\mathbf{K},\sigma}^+ A_{\mathbf{K},\sigma} \\
 & + \sum_{\mathbf{K}} \varepsilon_{\sigma'}(\mathbf{K} + \mathbf{q}) A_{\mathbf{K}+\mathbf{q},\sigma'}^+ A_{\mathbf{K}+\mathbf{q},\sigma'} + \sum_{\mathbf{K}} [G_{\sigma'\sigma}(\mathbf{q}) B_{\mathbf{q}} A_{\mathbf{K}+\mathbf{q},\sigma'}^+ A_{\mathbf{K},\sigma} + \text{H.c.}],
 \end{aligned} \tag{2.47}$$

where  $B_{\mathbf{q}}^+$  ( $B_{\mathbf{q}}$ ) is the creation (destruction) operator of the magnon with wave vector  $\mathbf{q}$  and frequency  $\omega_{\mathbf{q}}$  (index  $\mathbf{q}$  also includes polarization of the magnon);  $A_{\mathbf{K},\sigma}^+$  ( $A_{\mathbf{K},\sigma}$ ) is the creation (destruction) operator of the exciton with energy  $\varepsilon_{\sigma}(\mathbf{K})$  ( $\sigma$  is the index of the exciton band);  $A_{\mathbf{K}+\mathbf{q},\sigma'}^+$  and  $A_{\mathbf{K}+\mathbf{q},\sigma'}$  are similar operators for the excitons from the band with index  $\sigma'$ ;  $G_{\sigma'\sigma}(\mathbf{q})$  is the constant of exciton–magnon coupling. Indices  $\sigma$  and  $\sigma'$  distinguish the ground states of excitons of two different series, resulting from the binding into excitons of a hole and electron from the spin-polarized subband with spin projections  $\uparrow$  and  $\downarrow$ , respectively.

In the Hamiltonian (2.47) we omitted terms of the type  $B_{\mathbf{q}}^+ A_{\mathbf{K}+\mathbf{q},\sigma}^+ A_{\mathbf{K},\sigma}$  and  $B_{\mathbf{q},\sigma} A_{\mathbf{K},\sigma}^+ A_{\mathbf{K}+\mathbf{q},\sigma}$ , which are responsible for the processes of intraband scattering of excitons on magnons. The reason is that in the frequency range where the line of interband absorption of magnons by excitons has a maximum, the contribution from the processes of intraband scattering of excitons on magnons can be ignored. The Hamiltonian (2.47) also does not contain terms describing the interaction of excitons and magnons with the dissipative subsystems and the pumping subsystem that create the inversion of populations of exciton bands. As in Sect. 2.4, the pumping and the dissipative subsystems will be considered phenomenologically.

The equations of motion for the operators of the magnon field, exciton polarization, and the operators of the population difference of the states  $|\sigma'; \mathbf{K} + \mathbf{q}\rangle$  and  $|\sigma; \mathbf{K}\rangle$  of different bands have the form

$$\begin{aligned}
 \dot{B}_{\mathbf{q}} = & -(i\omega_{\mathbf{q}} + \varkappa) B_{\mathbf{q}} - \frac{i}{\hbar} G_{\sigma'\sigma}^*(\mathbf{q}) \sum_{\mathbf{K}} S^-(\sigma'\sigma | \mathbf{K}, \mathbf{q}), \\
 \dot{S}^-(\sigma'\sigma | \mathbf{K}, \mathbf{q}) = & -[i\omega_{\sigma'\sigma}(\mathbf{K}, \mathbf{q}) + \gamma_{\sigma'\sigma}] S^-(\sigma'\sigma | \mathbf{K}, \mathbf{q}) \\
 & + 2\frac{i}{\hbar} G_{\sigma'\sigma}(\mathbf{q}) B_{\mathbf{q}} S_z(\sigma'\sigma | \mathbf{K}, \mathbf{q}), \\
 \dot{S}_z(\sigma'\sigma | \mathbf{K}, \mathbf{q}) = & \frac{1}{T_1} \left[ \frac{1}{2} d_{\sigma'\sigma}^{(0)}(\mathbf{K}, \mathbf{q}) - S_z(\sigma'\sigma | \mathbf{K}, \mathbf{q}) \right] \\
 & + \frac{i}{\hbar} [G_{\sigma'\sigma}(\mathbf{q}) B_{\mathbf{q}} S^-(\sigma'\sigma | \mathbf{K}, \mathbf{q}) - G_{\sigma'\sigma}(\mathbf{q}) B_{\mathbf{q}} S^+(\sigma'\sigma | \mathbf{K}, \mathbf{q})], \\
 \dot{S}^+(\sigma'\sigma | \mathbf{K}, \mathbf{q}) = & (\dot{S}^-(\sigma'\sigma | \mathbf{K}, \mathbf{q}))^+, \\
 \dot{B}_{\mathbf{q}}^+ = & (\dot{B}_{\mathbf{q}})^+,
 \end{aligned} \tag{2.48}$$



where the effective spin operators are introduced:

$$\begin{aligned} S_z(\sigma'\sigma|\mathbf{K}, \mathbf{q}) &= \frac{1}{2}(A_{\mathbf{K}+\mathbf{q},\sigma'}^+ A_{\mathbf{K}+\mathbf{q},\sigma'} - A_{\mathbf{K},\sigma}^+ A_{\mathbf{K},\sigma}), \\ S^+(\sigma'\sigma|\mathbf{K}, \mathbf{q}) &= A_{\mathbf{K}+\mathbf{q},\sigma'}^+ A_{\mathbf{K},\sigma}, \\ S^-(\sigma'\sigma|\mathbf{K}, \mathbf{q}) &= A_{\mathbf{K},\sigma}^+ A_{\mathbf{K}+\mathbf{q},\sigma'} \end{aligned}$$

and the following designations are used:

$$\hbar\omega_{\sigma'\sigma}(\mathbf{K}, \mathbf{q}) = \varepsilon_{\sigma'}(\mathbf{K} + \mathbf{q}) - \varepsilon_{\sigma}(\mathbf{K}) = JSM(T)/M(0) + \frac{\hbar^2 q^2}{2m_{\text{ex}}} + \frac{\hbar^2 \mathbf{K}\mathbf{q}}{m_{\text{ex}}},$$

$\varkappa$  is the constant of magnon damping at the exciton–magnon interaction;  $\gamma_{\sigma'\sigma} = \frac{1}{2}(\gamma_{\sigma'} + \gamma_{\sigma})$ ;  $\hbar\gamma_{\sigma}$  and  $\hbar\gamma_{\sigma'}$  are the magnitudes of the washing away of the bands  $\sigma$  and  $\sigma'$ ;  $T_1$  is the time of the longitudinal relaxation of the excitons;  $d_{\sigma'\sigma}^{(0)}(\mathbf{K}, \mathbf{q})$  is the initial inverse population of the exciton bands.

In approaching the macrocompleted magnon mode ( $\langle B_{\mathbf{q}} \rangle = \sqrt{N_{\mathbf{q}}} e^{-i\Omega t}$ ,  $N_{\mathbf{q}}$  is the number of magnons in the mode), the solution of the system of nonlinear equations (2.48) by the method described in Sect. 2.4 leads to expressions for the constant  $\varkappa$  of magnon damping,

$$2\varkappa = \mathcal{G}_1 - \mathcal{G}_2 N_{\mathbf{q}}, \quad (2.49)$$

and for the shift of the frequency of generation  $\Omega$  relative to the frequency  $\omega_{\mathbf{q}}$  of the magnon in the absence of interaction with excitons,

$$\Omega - \omega_{\mathbf{q}} = (\Delta\Omega)_1 + N_{\mathbf{q}}(\Delta\Omega)_2, \quad (2.50)$$

which coincide with formulas (2.35) and (2.37), if we replace  $N$ ,  $g_{n'n}(0)$ ,  $\Gamma_{n'n}$ ,  $d_{n'n}^{(0)}(\mathbf{K})$ , and  $\omega_{n'n}(\mathbf{K})$  by  $N_{\mathbf{q}}$ ,  $G_{\sigma'\sigma}(\mathbf{q})$ ,  $\gamma_{\sigma'\sigma}$ ,  $d_{\sigma'\sigma}^{(0)}(\mathbf{K}, \mathbf{q})$ , and  $\omega_{\sigma'\sigma}(\mathbf{K}, \mathbf{q})$ . From these expressions it is seen that the condition of the self-excitation of the quantum generator of the magnons ( $\mathcal{G}_1 > 2\varkappa$ ) and the shift of the frequency of generation are determined by the function  $d_{\sigma'\sigma}^{(0)}(\mathbf{K}, \mathbf{q})$ , whose evident form depends on the method of pumping and the function of the distribution of excitons in the bands. For an equilibrium distribution of excitons we have

$$d_{\sigma'\sigma}^{(0)}(\mathbf{K}, \mathbf{q}) = \frac{8}{V}(\pi\alpha)^{3/2} e^{-\alpha K^2} (N_{\sigma'} e^{-\alpha(\mathbf{q}^2 + 2\mathbf{K}\mathbf{q})} - N_{\sigma}), \quad (2.51)$$

where  $N_{\sigma'}(N_{\sigma})$  is the full number of excitons in the band  $\sigma'(\sigma)$ .



After replacing in (2.49) and (2.50)  $\Omega$  by  $\omega_{\mathbf{q}}$  (on the same basis as in the case of IR laser) and using formula (2.51), we obtain

$$\begin{aligned}
 \mathcal{G}_1 &= 2 \left( \frac{\alpha}{\pi} \right)^{1/2} \hbar^{-2} \gamma_{\sigma'\sigma} |G_{\sigma'\sigma}(\mathbf{q})|^2 \left( \frac{m_{\text{ex}}}{\hbar q} \right)^2 (\tilde{N}_{\sigma'} I_2 - N_{\sigma} I_1), \\
 \mathcal{G}_2 &= 8 \left( \frac{\alpha}{\pi} \right)^{1/2} \hbar^{-4} \gamma_{\sigma'\sigma}^2 T_1 |G_{\sigma'\sigma}(\mathbf{q})|^4 \left( \frac{m_{\text{ex}}}{\hbar q} \right)^4 (\tilde{N}_{\sigma'} I_4 - N_{\sigma} I_3), \\
 (\Delta\Omega)_1 &= - \left( \frac{\alpha}{\pi} \right)^{1/2} \hbar^{-2} |G_{\sigma'\sigma}(\mathbf{q})|^2 \frac{m_{\text{ex}}}{\hbar q} [C_{\sigma'\sigma} (\tilde{N}_{\sigma'} I_2 - N_{\sigma} I_1) \\
 &\quad - (\tilde{N}_{\sigma'} I_6 - N_{\sigma} I_5)], \\
 (\Delta\Omega)_2 &= \left( \frac{\alpha}{\pi} \right)^{1/2} \hbar^{-4} |G_{\sigma'\sigma}(\mathbf{q})|^4 \gamma_{\sigma'\sigma} T_1 \left( \frac{m_{\text{ex}}}{\hbar q} \right)^3 \\
 &\quad \times [C_{\sigma'\sigma} (\tilde{N}_{\sigma'} I_4 - N_{\sigma} I_3) - (\tilde{N}_{\sigma'} I_8 - N_{\sigma} I_7)],
 \end{aligned} \tag{2.52}$$

where

$$I_l = \int_{-\infty}^{\infty} \frac{K_z^{\mu} \exp\{-\alpha(K_z^2 + 2\beta q K_z)\}}{[a_{\sigma'\sigma}^2 + (C_{\sigma'\sigma} + K_z)^2]^{\nu}} dK_z. \tag{2.53}$$

For  $l = 1, 2, \dots, 8$ , the triples of numbers  $\mu, \beta, \nu$  have, respectively, the values 001, 011, 002, 012, 101, 111, 102, 112.

In (2.52) and (2.53) we use the designations

$$\begin{aligned}
 a_{\sigma'\sigma} &= \frac{m_{\text{ex}}}{\hbar q} \gamma_{\sigma'\sigma}, \quad \tilde{N}_{\sigma'} = N_{\sigma'} e^{-\alpha q^2}, \\
 C_{\sigma'\sigma} &= \frac{q}{2} - \frac{m_{\text{ex}} v}{\hbar} + \frac{m_{\text{ex}}}{\hbar^2 q} J S M(T)/M(0),
 \end{aligned} \tag{2.54}$$

where  $K_z$  is the projection of the exciton wave vector on the direction  $\mathbf{q}$ .

The integral of type  $I_1$  ( $\mu = \beta = 0; \nu = 1$ ) from (2.53) is sometimes found in other problems of microwave spectroscopy in research on the forms of resonance lines, in determining a function of Voigt's form [12]. In Chap. 3 the connection of the integrals  $I_l$  with the probability function during the consideration of the exciton-phonon interaction will be shown, for which the dependence on the wave vector of the phonon is as essential as the dependence of the exciton-magnon interaction on the wave vector of the magnon discussed in this section. Here we note that, as a consequence of the large conduction band splitting due to the interaction of free charge carriers with the localized magnetic moments (for example, for the europium chalcogenides  $J S \sim 0.5$  eV [303]), the distance among the lowest exciton bands  $\sigma$  and  $\sigma'$ , belonging to different series, exceeds the kinetic energy of the excitons which move with the speed of the spin wave:

$$J S M(T)/M(0) > \frac{m_{\text{ex}} v_s^2}{2}.$$



Therefore, during the intraserial transitions with the absorption (emission) of magnons there are the excitons from the lowest band having wave vectors that are closed in a sphere of radius  $K_c = C_{\sigma'\sigma}$ , where  $C_{\sigma'\sigma}$  is determined by (2.54). Note that these excitons do not take part in the exciton–magnon interaction due to the law of energy and impulse conservation. This hampers the observation of the absorption of the magnons by the excitons because of the necessity to create excitons in the lowest band with large values of the wave vector  $K > K_c$ . However, the stimulated radiation of coherent magnons is possible during the optical creation of excitons in the state with  $\mathbf{K} = \mathbf{Q}$  ( $\mathbf{Q}$  is the wave vector of the photon) of the upper band. Under conditions of an inverted exciton population of exciton bands, coherent magnons with wave vectors  $\mathbf{q} \geq \mathbf{K}_c - \mathbf{Q}$  are emitted. If the width of the lowest band does not exceed the distance between bands  $\sigma$  and  $\sigma'$ , then if the condition  $aK_c \leq \pi$  is satisfied, coherent magnons with large wave vectors are generated, their length being the order of the distance from the center to the frontier of the Brillouin zone.

The authors of the work [305] displayed the resonance behavior of magnetic circular dichroism and the Faraday effect in the magnetic ordered phase of the single crystal  $\text{CdCr}_2\text{Se}_4$  in the exciton region of the spectrum (during the excitation of photons with the energy  $E = 1\text{--}1.5$  eV exceeding the energy of the “red-shifted” edge of the absorption). In samples with a high content of indium impurity ( $\sim 4$  weights %) the resonance peaks related to the right- and left-circular polarized light were not observed. The Faraday effect was also suppressed sharply in these samples. Thus we expect that, for the experimental observation of the effect of generation of coherent magnons at optical excitation of magnetic semiconductors, it is necessary to have sufficiently pure crystals.

Features of the stoichiometry of crystals may be indicated using the small EPR linewidth in the region of the wide minimum on the temperature dependence  $\Delta H(T)$  in the paramagnetic phase. With  $T = T_{\min}$  ( $T_{\min}$  is the temperature at which the function  $\Delta H(T)$  achieves the minimum) the lowest value  $\Delta H(T_{\min})$  corresponds to the lowest deviation from stoichiometry [20, 306]. In [20] it was shown that the experimentally observed temperature dependence of the EPR linewidth of monocrystals  $\text{CdCr}_2\text{S}_4$ , synthesized by the method of gas-transport reactions, is well approximated at  $T > T_{\min}$  by the equation

$$\Delta H(T) = \Delta H(T_{\min}) + A \exp(-\theta/T)$$

with the parameters  $\theta = 1210$  K and  $A = 1300$  Oe. A noncontradictory explanation of the exponential dependence of  $\Delta H(T)$  on the indicated values  $\theta$  and  $A$  was given on the basis of the account of Raman processes with participation of the localized phonons in the conditions when  $\theta > T_D$  ( $T_D$  is the Debye temperature; for  $\text{CdCr}_2\text{S}_4$   $T_D = 415$  K [307]), leading to reorientation of the spin of the  $\text{Cr}^{3+}$  ion. Local vibrations are performed near the locations of rapidly relaxing paramagnetic impurity centers (the role of the latter is played by the ions of the two-valent chromium, which appear because of the deviation of the composition of  $\text{CdCr}_2\text{S}_4$  from stoichiometry with the formation of a sulfur deficit [308]). That is why the value of  $\Delta H$  in the



domain of the wide minimum (near  $T_{\min}$ ) indicates the degree of nonstoichiometry of a magnetic semiconductor.

## 2.6 Exciton Paraelectric Resonance

Paraelectric resonance (PER) as a method of investigation of the impurity centers in solids with proper electric moments was proposed in [41]. The first experiments in this field (PER of dipolar molecules) were described in [309]. Substitutional impurity ions, shifted from their equilibrium positions in the lattice nodes (“noncentral” ions), can be investigated by PER method. The movement of these centers in a crystal is limited by the domain of their location and involves tunneling through the potential barriers. The first information on the observation of PER of noncentral ions was presented in [310]. An analysis of the results of the PER investigation of noncentral ions is given by Deigen and Glinchuk [42].

With PER selective absorption of the energy of an alternative electric field by a system of electric dipoles in the external constant electric field takes place. The directed deformation of the crystal [311] is applied along with the external constant electric field to remove the degeneration of the energy levels of the paraelectric system. The energy of the alternative field is transmitted by the resonance to the system of the electric dipoles, which leads to violation of its thermodynamic equilibrium. The latter is restored by the transmission of an abundance of absorbed energy to the lattice by dipole–lattice relaxation.

In some cases paraelectric systems provide perspective for practical applications in quantum electronics and low-temperature techniques [311]. For this reason, and because the optical electric dipole transitions between some of the states of paraelectric systems are forbidden by the selection rules (which hinders the study of these states by the usual optical methods), expanding the number of objects that can be investigated by the PER method is of interest. To this range of objects we can attribute Wannier–Mott excitons in semiconductors, regardless of the fact that, in contrast to paraelectric centers, the excitons possess translational symmetry. Exciton paraelectric resonance (ExPR) was studied theoretically in [170, 279–282].

We shall consider the degenerate exciton levels that are split in a constant electric field  $\mathbf{E}_0$ , where the magnitude of the splitting  $\Delta(\mathbf{E}_0)$  is in the microwave range. The transitions between split components are excited by the electric component of the microwave field (ExPR). The experimental conditions for the ExPR observations are more favorable in crystals without a center of inversion, in which  $\Delta(\mathbf{E}_0) \sim E_0$  may be expected. For this the exciton level must be orbitally degenerated, and its states must be characterized by different values of the proper or induced electric dipole moment. The exciton states that are transformed according to the twofold irreducible representations of the point groups of symmetry  $D_3$  and  $C_{3v}$  or to the threefold representations of the symmetry groups  $T_d$  and  $O$  satisfy these conditions. Doubly degenerate exciton levels are not split by the electric field, if the corresponding exciton states are transformed according to the twofold irreducible representations



of the symmetry point groups  $C_3$ ,  $S_4$ ,  $S_6$ , and  $T$ . This is a consequence of time-reversal symmetry.

Linear Stark splitting should show, in particular, the energy levels corresponding to exciton states formed from electron states of the lowest conduction band  $\Gamma_6$  and hole states of the upper valence band  $\Gamma_5$ , which is split by the spin-orbital interaction into subbands  $\Gamma_7$  and  $\Gamma_8$  in the crystal field of symmetry  $T_d$ . It relates, for example, to the dipole-active absorption line of orthoexciton  $1S(\Gamma_5)$ , formed by an electron from the  $\Gamma_6$  band and a hole from the subband  $\Gamma_7$  and to the lines as  $1S(\Gamma_4)$  and  $1S(\Gamma_5)$ , corresponding to the exciton formed by an electron from the  $\Gamma_6$  band and a hole from the  $\Gamma_8$  subband in the crystals CuCl, CuBr, and CuI [312]. The linear Stark effect has been observed in the electroabsorption on excitons in CuCl [313].

Other objects in which it is possible to observe the linear Stark effect on excitons are semiconductors of type  $A_2B_6$  and  $A_3B_5$  with the structure of zinc blende: ZnS, ZnSe, ZnTe, CdTe and GaP, GaAs, InP.

The absence of a center of inversion does not guarantee the linear splitting of the exciton level by the electric field. For example, in crystals with  $C_{6v}$  symmetry, the  $\Gamma_5$  and  $\Gamma_6$  states [314] at comparatively small electric fields are split quadratically on the field. This results from general theoretical-group reasons, and it is confirmed on the basis of experiments for CdS by Thomas and Hopfield [315].

The exciton level splittings necessary for observation of ExPR may also be achieved in crystals that possess a center of inversion. In this case in second-order perturbation theory  $\Delta(\mathbf{E}_0) \sim E_0^2$ . We shall select for consideration ExPR, in the presence of a center of inversion, for triply degenerate quadrupole-active level  $1S(\Gamma_5^+)$  of the yellow exciton series of crystal  $\text{Cu}_2\text{O}$ . Level  $1S(\Gamma_5^+)$  is probably suitable for the ExPR observation, because it is deep and allows us to apply high electric fields without essential self-ionization of the exciton state. This level is sufficiently narrow and isolated from other levels. For the calculation of  $\Delta(\mathbf{E}_0)$  we shall use the wave functions of first-order perturbation theory, taking into consideration the mixing under the action of the electric field of the state  $\Gamma_5^+$  with the excited states of the type  $\Gamma_2^-$ ,  $\Gamma_3^-$ ,  $\Gamma_4^-$  and  $\Gamma_5^-$ . At  $\mathbf{E}_0 \parallel \langle 1\bar{1}0 \rangle$  the corrections of the second order to the energy of the components of the split level  $1S(\Gamma_5^+)$ , where it mixes in the constant electric field only with the states  $n = 2$  of the yellow exciton series [316], are

$$\begin{aligned}\varepsilon_{A_1} &= E_0^2 \left( \frac{D_1^2}{\delta_1} + \frac{D_2^2}{\delta_2} + \frac{D_2'^2}{\delta_2'} \right), \\ \varepsilon_{A_2} &= E_0^2 \left( \frac{D_2^2}{\delta_2} + \frac{D_2'^2}{\delta_2'} + \frac{3}{2} \cdot \frac{|D_4|^2}{\delta_4} \right), \\ \varepsilon_{B_2} &= E_0^2 \left( \frac{D_1^2}{\delta_1} + \frac{D_3^2}{\delta_3} + \frac{1}{2} \cdot \frac{|D_4|^2}{\delta_4} \right),\end{aligned}\tag{2.55}$$

where  $\delta_i = \varepsilon_{\Gamma_5^+(n=1)}^0 - \varepsilon_{\Gamma_j^-(n=2)}^0$ ,  $i$  equal to 1, 2, 3, 4 respectively for  $j$ , which is equal to 4, 5, 2, 3;  $A_1$ ,  $A_2$  and  $B_2$  are irreducible representations of the symmetry



point group  $C_{2v}$  [127]. The terms  $D_2^2/\delta_2$  and  $D_2'^2/\delta_2'$  reflect the fact that for  $n = 2$  there are two different states of type  $\Gamma_5^-$ .

Matrix elements  $D_i$  of the electric dipole moment of transition between states  $\Gamma_5^+$  and  $\Gamma_j^- = \Gamma_4^-, \Gamma_5^-, \Gamma_2^-, \Gamma_3^-$  have the form

$$D_i = e \langle \Psi_{\Gamma_5^+, j_1}^0 | \sum_k r_{kj_2} | \Psi_{\Gamma_j^-, j_3}^0 \rangle, \quad (2.56)$$

where  $r_{kj_2}$  is the  $j_2$ -projection of the radius vector of the  $k$ th electron;  $j_1, j_2$  and  $j_3$  are selected as  $D_i \neq 0$ . For example, for  $\Gamma_j^- = \Gamma_4^-$ ,  $j_1 = 1, j_2 = 2, j_3 = 3$ .

In order to account for mixing of state  $\Gamma_5^+$  with the odd excited states of all terms of the exciton series, it is sufficient to replace  $D_i^2 \delta_i^{-1}$  in (2.55) by  $\sum_{fn} D_{i,n}^2 \delta_{i,n,f}^{-1}$ , where  $f$  is the number of representations  $\Gamma_j$  for the given  $n$ .

The burning of the exciton absorption in the dipole approximation to the level  $\Gamma_5^+$  in the electric field is affected by the mixing of state  $\Gamma_5^+$  only with states of type  $\Gamma_4^-$ . In contrast, in the splitting of the level  $\Gamma_5^+$  in the electric field, the mixing with other states contributes, and these states are transformed according to odd representations. As can be seen from (2.55), it is not possible to achieve a complete splitting without taking into account the mixing with the states of type  $\Gamma_2^-, \Gamma_3^-$ , and  $\Gamma_5^-$ . Since Stark splittings depend on  $\delta_i^{-1}$  linearly, the line  $1S(\Gamma_5^+)$  of the yellow exciton series of the  $\text{Cu}_2\text{O}$  crystal in the electric field must show, along with the splitting, a shift to the longer wavelengths of the spectrum. The latter is in accordance with the experiments of Nikitine et al. [317]. However, the change of the energy gap in the electric field also leads to a shift of exciton levels.

Estimations according to the formulas (2.55) in a one-electron approximation on the simple exciton wave functions taking into account orbital degeneration of the valence band with  $r_{\text{ex}(n=1)} = 10 \text{ \AA}$ ,  $r_{\text{ex}(n=2)} = 30\text{--}40 \text{ \AA}$ ,  $\delta_i = -0.12 \text{ eV}$ , and  $E_0 = 160 \text{ kV/cm}$  lead to  $\Delta(E_0) \approx (1\text{--}3) \cdot 10^{-4} \text{ eV}$ , which corresponds to the value  $\Delta(E_0)$ , estimated in the experiments on the burning and amplification of the absorption on level  $\Gamma_5^+$  in the electric field [316]. Stark splitting of the line  $1S(\Gamma_5^+)$  in the  $\text{Cu}_2\text{O}$  crystal seems to be of the order of the width of exciton level  $1S(\Gamma_5^+)$  at a temperature of 4.2 K in the absence of the electric field ( $\Delta v_{1/2} = 2.3 \cdot 10^{-4} \text{ eV}$  [317]) and may be measured by the method of modulational spectroscopy, applying synchronous detection [318].

We shall determine the amplitudes of the paraelectric transitions between the components of level  $\Gamma_5^+$  with the assumption that the main contribution to the width of the Stark sublevels is caused by exciton–phonon collisions and the width of separate Stark components is not bigger than the width of the exciton line in the absence of an electric field. Matrix elements of the transitions between the components  $\Gamma$  and  $\Gamma'$  of level  $\Gamma_5^+$  having been split in the electric field for different polarizations  $[hkl]$  of the incident microwave radiation are determined by the expression

$$P_{\Gamma\Gamma'}^{[hkl]} = e \langle \Psi_{\Gamma} | \sum_i \mathbf{r}_i | \Psi_{\Gamma'} \rangle \mathbf{E}_1^{[hkl]},$$



where  $\Psi_\Gamma$  and  $\Psi_{\Gamma'}$  are the wave functions of the exciton on sublevels  $\Gamma$  and  $\Gamma'$  in first-order perturbation theory (taking into account the mixing with the levels  $\Gamma_2^-$ ,  $\Gamma_3^-$ ,  $\Gamma_4^-$ , and  $\Gamma_5^-$  for  $n \geq 2$ ), and  $E_1$  is the amplitude of the electric component of the microwave.

For some symmetry directions in the crystal we obtain

$$\begin{aligned}
 \mathbf{E}_0 \parallel [1\bar{1}0] \quad P_{A_1 B_2}^{[001]} &= \frac{E_1}{E_0} (\varepsilon_{B_2} - \varepsilon_{A_2}), \\
 \mathbf{E}_0 \parallel [001] \quad P_{A_2 B_2}^{[110]} &= \frac{E_1}{E_0} (\varepsilon_{A_2} + \varepsilon_{B_2} - 2\varepsilon_{A_1}), \\
 P_{\Delta'_2 \Delta_5}^{[1\bar{1}0]} &= P_{\Delta'_2 \Delta_5}^{[110]} = P_{A_1 B_2}^{[001]}, \\
 \mathbf{E}_0 \parallel [111] \quad P_{A_1 A_3}^{[1\bar{1}0]} &= P_{A_1 A_3}^{[11\bar{2}]} = \frac{E_1}{3E_0} (3\varepsilon_{B_2} + \varepsilon_{A_2} - 4\varepsilon_{A_1})
 \end{aligned} \tag{2.57}$$

where  $\Delta'_2$ ,  $\Delta_5$ , and  $A_j$  are the irreducible representations of the symmetry groups  $C_{4v}$  and  $C_{3v}$  [319]. The designations  $A_1$ ,  $A_2$ ,  $B_2$ ,  $B_1$  correspond to  $E_1$ ,  $E_2$ ,  $E_3$ ,  $E_4$  from [319]. The other matrix elements for the directions  $\mathbf{E}_0$  indicated in (2.57) are equal to 0. Therefore, in the adopted approximation  $P_{\Gamma\Gamma'} = 0$  at  $\mathbf{E}_1 \parallel \mathbf{E}_0$  for all directions of the electric field  $\mathbf{E}_0$  and for the ExPR that we consider, the condition of the perpendicularity of the field, consisting in the fact that the component  $\mathbf{E}_1$  is perpendicular to  $\mathbf{E}_0$ , is performed.

The absorption of the energy of the alternative electric field may be used for detecting and investigating the optically inactive levels. One such level is  $1S(\Gamma_2^+)$  of the yellow exciton series of the  $\text{Cu}_2\text{O}$  crystal. The nonzero matrix elements of the transitions between the components of the levels  $\Gamma_5^+$  and  $\Gamma_2^+$  are

$$P_{A_1 B_1}^{[110]} = -P_{A_2 B_1}^{[001]} = P_{\Delta_2 \Delta_5}^{[1\bar{1}0]} = P_{A_2 A_3}^{[1\bar{1}0]} = -P_{A_2 A_3}^{[11\bar{2}]} = e^2 E_0 E_1 D_2 D_5 \left( \frac{1}{\delta_5} - \frac{1}{\delta_2} \right), \tag{2.58}$$

where  $\delta_5 = \varepsilon_{\Gamma_2^+(n=1)}^0 - \varepsilon_{\Gamma_5^-(n=2)}^0$ ,  $D_5$  is the matrix element of the electric dipole moment of the transition, similar to  $D_i$  from (2.56), between states  $\Gamma_2^+$  and  $\Gamma_5^-$ , and  $B_1$ ,  $\Delta_2$ , and  $A_2$  are the irreducible representations according to which state  $\Gamma_2^+$  is transformed with the decrease of the symmetry of the crystal up to  $C_{2v}$ ,  $C_{4v}$ , and  $C_{3v}$  that takes place, respectively, at  $\mathbf{E}_0 \parallel [1\bar{1}0]$ ,  $\mathbf{E}_0 \parallel [001]$ , and  $\mathbf{E}_0 \parallel [111]$  [319]. It is seen from (2.58) that the condition of the perpendicularity of the fields is performed for the transitions between states  $\Gamma_2^+$  and  $\Gamma_5^-$ .

The expressions (2.57) and (2.58) for  $P_{\Gamma\Gamma'}^{[hkl]}$  are obtained without the specificity of the type of exciton wave functions. The latter enter only in the matrix elements  $D_i$ . In accordance with the formulas (2.55) the matrix elements  $D_i$  can be determined from the experimental data for the splittings and the shifts of exciton lines in the electric field. If this is possible, then one can select optimal conditions for the ExPR observation on the excitons, immediately resulting from the experimental data. The selection of optimal conditions for the ExPR observation can also be



performed if the data on the polarizability of the excitons are known. The large diamagnetism [320] of the excitons and their large polarizability [321] cause high oscillator strengths for the paraelectric transitions. The values  $D_i$  can also be determined from the experiments on burning and amplification of exciton lines of light absorption in an electric field, or estimated by means of direct theoretical calculations in the one-electron approximation [281, 282, 316].

We shall estimate the power absorbed by the unit volume of the crystal at the ExPR transition from level  $A_1$  to level  $B_2$  by the formula

$$W_{A_1 B_2} = \frac{\pi}{2\hbar} (N_{A_1} - N_{B_2}) \omega_{A_1 B_2} \left( \frac{E_1}{E_0} \right)^2 (\varepsilon_{B_2} - \varepsilon_{A_1})^2 g(\omega),$$

where  $\omega_{A_1 B_2}$  is the frequency of transition,  $N_{A_1}$  and  $N_{B_2}$  are the populations of levels  $A_1$  and  $B_2$ , and  $g(\omega)$  is the function of the form of the ExPR line.

In the high temperature approximation ( $\varepsilon_{B_2} - \varepsilon_{A_1} \ll k_0 T$ ) at  $\varepsilon_{B_2} - \varepsilon_{A_1} = 2 \text{ cm}^{-1}$ ,  $T = 77 \text{ K}$ ,  $E_0 = 160 \text{ kV/cm}$ , concentration of excitons  $n_{\text{ex}} = 10^{15} \text{ cm}^{-3}$ , and with the supposition that the ExPR linewidth is approximately equal to the resonance frequency, we obtain  $W_{A_1 B_2} \approx 5 \cdot 10^{-8} \text{ W/cm}^3$ . Let us remark that the fluctuations of the power of a microwave generator are less in comparison with the estimated value of the power absorbed by a unit of the volume of the substance with ExPR transitions on excitons. For example, for a klystron of 3 cm spectral range, the level of noise in the 2.5 MHz band, shifted with respect to the fundamental frequency of the klystron on the value of 30 MHz, is  $10^{-11}$ – $10^{-12} \text{ W}$  and sharply decreases with an increase of the intermediate frequency from 30 MHz to 90 MHz [12]. Therefore, the experimental detection of ExPR in semiconductors is feasible.

In relatively pure crystals, in which the concentration of impurities is  $n_{\text{imp}} \lesssim 10^{16} \text{ cm}^{-3}$ , the width of the exciton levels is determined mainly by exciton–phonon and exciton–exciton collisions. In this case, the time of the free run of the exciton at low temperatures is  $\tau_{\text{path}} \sim 10^{-10}$ – $10^{-9} \text{ s}$  [171]. Consequently, ExPR may be observed on the frequencies  $\omega > 10^9$ – $10^{10} \text{ s}^{-1}$ .

The form of the ExPR line is also determined by exciton–phonon and exciton–exciton interaction. These interactions are as effective as dipole–lattice and dipole–dipole interaction for localized electric dipoles (for  $\text{OH}^-$  dipoles in the KCl crystal the electric dipole–lattice relaxation time at  $T = 11 \text{ K}$  is equal to  $10^{-11} \text{ s}$ ) [309], but the electric dipole–dipole relaxation time at 2.4 K and  $n_{\text{OH}^-} = 3 \cdot 10^{16} \text{ cm}^{-3}$  is  $10^{-10} \text{ s}$  [311]. Similarly as with the local centers we could introduce for the excitons the concepts of electric dipole–lattice and dipole–dipole interaction indicated above. However, an important peculiarity of excitons distinguishing them from the local centers is the possibility of intraband exciton–phonon scattering.

Absorption of the energy of the electric field by excitons can also occur and then, when the processes of the paraelectric relaxation are not effective. This possibility is influenced by the presence of the difference of populations of exciton levels under conditions of optical pumping. The numbers of filling excitons on the split electric field sublevels are determined by pumping and depend both on the processes of



relaxation between sublevels and the lifetime of the excitons on these sublevels relative to the processes of annihilation.

## 2.7 Isotopic Shift of Exciton Paraelectric Resonance in $\text{Cu}_2\text{O}$ Crystals

The PER on excitons considered in the preceding section may be both intraserial (by which ExPR transitions take place between the states belonging to one exciton series) and interserial. An interesting peculiarity of interserial ExPR is the possibility for it to manifest isotopic effects. Qualitatively it may be explained on the basis of the existing experimental data on the isotopic shift of the exciton lines in the optical spectrum of  $\text{Cu}_2\text{O}$  crystals. According to [322–324], with isotopic substitution of the isotope  $^{16}\text{O}$  by  $^{18}\text{O}$  in the crystal  $\text{Cu}_2\text{O}$  a shift of all the lines of the exciton absorption takes place. Each of all four exciton series are shifted as a whole without a significant change of the Rydberg constant (the yellow and green series are shifted to shorter wavelengths of the spectrum, the dark blue and light blue series toward longer wavelengths of the spectrum). In the substituted crystal the energy of the longitudinal optical phonon of symmetry  $\Gamma_4^-$ , caused by the shift of the oxygen ions, decreases by  $25 \text{ cm}^{-1}$ . Changes of the lattice constant are not detected.

As isotopic substitution leads to a shift of the exciton series as a whole, it will not be displayed by intraserial ExPR, but it may be detected in the spectra of interserial ExPR, if the shift of the ExPR line is large enough for the measurement. For excitons of the yellow and green series of  $\text{Cu}_2\text{O}$  crystals, the isotopic shift of the interserial ExPR lines, as will be shown below, occurs in the short-wavelength region of the spectrum and has a magnitude  $\sim 2.3 \text{ cm}^{-1}$  that may be easily measured.

The basis for the theoretical calculation of the considered effect of the isotopic shift of the interserial ExPR lines is the method of canonical transformation, which helps us to obtain renormalized energies of the electrons and holes due to the interaction with phonons before and after the isotopic substitution.

The Hamiltonian of the system of electrons and holes interacting with the phonons has the form

$$H = H_0 + H_1 + H_2, \quad (2.59)$$

where

$$\begin{aligned} H_0 = & \sum_{kl} E_{\Gamma_6^+ l}(\mathbf{k}) a_{\mathbf{k}\Gamma_6^+ l}^+ a_{\mathbf{k}\Gamma_6^+ l} + \sum_{km} E_{\Gamma_8^- m}(\mathbf{k}) a_{\mathbf{k}\Gamma_8^- m}^+ a_{\mathbf{k}\Gamma_8^- m} \\ & + \sum_{kn} E_{\Gamma_7^{+*} n}(\mathbf{k}) B_{\mathbf{k}\Gamma_7^{+*} n}^+ B_{\mathbf{k}\Gamma_7^{+*} n} + \sum_{ks} E_{\Gamma_8^{+*} s}(\mathbf{k}) B_{\mathbf{k}\Gamma_8^{+*} s}^+ B_{\mathbf{k}\Gamma_8^{+*} s} \\ & + \sum_{\mathbf{q}} \hbar\omega_0 C_{\mathbf{q}}^+ C_{\mathbf{q}}, \end{aligned} \quad (2.60)$$



$$\begin{aligned}
H_1 = & \frac{i}{\sqrt{N}} \sum_{\mathbf{k}\mathbf{q}j,l} \{ \theta_e(\mathbf{k}, \mathbf{q}; j, l) a_{\mathbf{k}+\mathbf{q}, \Gamma_6^+ j}^+ a_{\mathbf{k}\Gamma_8^- l} \\
& + \theta_e^*(\mathbf{k}, -\mathbf{q}; j, l) a_{\mathbf{k}\Gamma_8^- l}^+ a_{\mathbf{k}-\mathbf{q}, \Gamma_6^+ j} - \theta_h(\mathbf{k}, \mathbf{q}; j, l) B_{-\mathbf{k}\Gamma_8^{+*} l}^+ B_{-\mathbf{k}-\mathbf{q}, \Gamma_7^{+*} j} \\
& - \theta_h^*(\mathbf{k}, -\mathbf{q}; j, l) B_{-\mathbf{k}+\mathbf{q}, \Gamma_7^{+*} j}^+ B_{-\mathbf{k}\Gamma_8^{+*} l} \} (C_{\mathbf{q}} - C_{-\mathbf{q}}^+), \\
H_2 = & \frac{i}{\sqrt{N}} \sum_{\mathbf{k}\mathbf{q}j} \vartheta(\mathbf{q}) (a_{\mathbf{k}+\mathbf{q}, \Gamma_6^+ j}^+ a_{\mathbf{k}\Gamma_6^+ j} + a_{\mathbf{k}+\mathbf{q}, \Gamma_8^- j}^+ a_{\mathbf{k}\Gamma_8^- j} \\
& - B_{-\mathbf{k}\Gamma_7^{+*} j}^+ B_{-\mathbf{k}-\mathbf{q}, \Gamma_7^{+*} j} - B_{-\mathbf{k}\Gamma_8^{+*} j}^+ B_{-\mathbf{k}-\mathbf{q}, \Gamma_8^{+*} j}) (C_{\mathbf{q}} - C_{-\mathbf{q}}^+). \quad (2.61)
\end{aligned}$$

In (2.60)–(2.61)  $C_{\mathbf{q}}^+$  is the creation operator of the longitudinal optical phonon with wave vector  $\mathbf{q}$ ,  $a_{\mathbf{k}\Gamma\gamma}^+$  and  $B_{\mathbf{k}\Gamma^*\gamma}^+$  are, respectively, the creation operators of the electron and hole with wave vector  $\mathbf{k}$  in the band characterized by the irreducible representation  $\Gamma$ ;  $E_{\Gamma\gamma}(\mathbf{k})$  and  $E_{\Gamma^*\gamma}(\mathbf{k})$  are the energy of the electron and hole in the corresponding bands,  $\gamma$  is the line of representation, and  $N$  is the number of atoms in the lattice. By  $\vartheta(\mathbf{q})$  and  $\theta_{e(h)}(\mathbf{k}, \mathbf{q}; j, l)$  we designate the Fourier transform of the energy of the electron (hole)–phonon interaction for the cases of intraband and interband scattering, respectively. The function  $\vartheta(\mathbf{q})$  has the form (only the Fröhlich interaction is taken into consideration)

$$\vartheta(\mathbf{q}) = (2\pi e^2 \hbar \omega_0 / \varepsilon^* \mathcal{V}_0 q^2)^{1/2} \langle \Gamma\gamma, \mathbf{k}_1 | e^{i\mathbf{q}\mathbf{r}} | \Gamma\gamma, \mathbf{k}_2 \rangle,$$

where  $1/\varepsilon^* = 1/\varepsilon_\infty - 1/\varepsilon_0$ ,  $\omega_0$  is the frequency of the longitudinal optical phonon, and  $\mathcal{V}_0$  is the volume of the elementary cell. The form of the functions  $\theta_e(\mathbf{k}, \mathbf{q}; j, l)$  and  $\theta_h(\mathbf{k}, \mathbf{q}; j, l)$  must be determined.

Electron (hole)–phonon interaction is eliminated by means of the Fröhlich unitary transformation of the Hamiltonian (2.59)

$$\tilde{H} = e^{-S} H e^S.$$

The operator  $S$  satisfies the condition

$$[H_0, S] + H_1 = 0.$$

After averaging on the phonon subsystem we obtain the effective Hamiltonian of the electrons and holes with the renormalized energy. At  $T = 0$  the expressions for the energy of electrons in the bands  $\Gamma_6^+$ ,  $\Gamma_8^-$  and holes in the bands  $\Gamma_7^+$  and  $\Gamma_8^+$ , renormalized by intraband and interband scattering on phonons, can be presented in the form

$$\tilde{E}_{\Gamma_v}(\mathbf{k}) = E_{\Gamma_v}(\mathbf{k}) + \Delta_{\Gamma_v}^{\text{intra}} + \Delta_{\Gamma_v}^{\text{inter}}, \quad (2.62)$$

where  $\Gamma = \Gamma_6^+$ ,  $\Gamma_8^-$ ,  $\Gamma_7^+$ , and  $\Gamma_8^+$ ;  $\Delta_{\Gamma_v}^{\text{intra}}$  and  $\Delta_{\Gamma_v}^{\text{inter}}$  are energy corrections influenced, respectively, by intra- and interband scattering of electrons and holes on the phonons.



The energy correction  $\Delta_{\Gamma_v}^{\text{intra}}$  from (2.62) is determined by the expression

$$\Delta_{\Gamma_v}^{\text{intra}} = -\frac{1}{N} \sum_{\mathbf{q}} \frac{|\vartheta(\mathbf{q})|^2}{E_{\Gamma_v}(\mathbf{k} + \mathbf{q}) - E_{\Gamma_v}(\mathbf{k}) + \hbar\omega_0},$$

which in the approximation [325–327]

$$\frac{\hbar^2(\mathbf{k}\mathbf{q})}{m_{\Gamma_v}(\hbar\omega_0 + \hbar^2 q^2/2m_{\Gamma_v})} \ll 1$$

is transformed to

$$\Delta_{\Gamma_v}^{\text{intra}} = -\frac{1}{2} \frac{e^2}{\varepsilon^*} U_{\Gamma_v}. \quad (2.63)$$

Here  $U_{\Gamma_v} = \sqrt{2m_{\Gamma_v}\omega_0/\hbar}$  is the inverse polaron radius and  $m_{\Gamma_v}$  is the mass of the band electron (hole).

Corrections influenced by interband scattering have the form

$$\begin{aligned} \Delta_{\Gamma_6^+,j}^{\text{inter}} &= -\frac{1}{N} \sum_{\mathbf{q}} \frac{|\theta_e(\mathbf{k}, \mathbf{q}; j, m)|^2}{E_{\Gamma_8^-}(\mathbf{k} + \mathbf{q}) - E_{\Gamma_6^+}(\mathbf{k}) + \hbar\omega_0}, \\ \Delta_{\Gamma_8^-,j}^{\text{inter}} &= \frac{1}{N} \sum_{\mathbf{q}m} \frac{|\theta_e(\mathbf{k}, \mathbf{q}; j, m)|^2}{E_{\Gamma_8^-}(\mathbf{k}) - E_{\Gamma_6^+}(\mathbf{k} + \mathbf{q}) - \hbar\omega_0}, \\ \Delta_{\Gamma_7^+,j}^{\text{inter}} &= \frac{1}{N} \sum_{\mathbf{q}m} \frac{|\theta_h(\mathbf{k}, \mathbf{q}; j, m)|^2}{E_{\Gamma_8^+}(\mathbf{k} - \mathbf{q}) - E_{\Gamma_7^+}(\mathbf{k}) + \hbar\omega_0}, \\ \Delta_{\Gamma_8^{+*},j}^{\text{inter}} &= -\frac{1}{N} \sum_{\mathbf{q}m} \frac{|\theta_h(\mathbf{k}, \mathbf{q}; j, m)|^2}{E_{\Gamma_8^+}(\mathbf{k}) - E_{\Gamma_7^+}(\mathbf{k} - \mathbf{q}) - \hbar\omega_0}, \end{aligned} \quad (2.64)$$

where

$$\theta_{e(h)}(\mathbf{k}, \mathbf{q}; j, m) = \left( \frac{2\pi e^2 \hbar \omega_0}{\mathcal{V}_0 \varepsilon^* q^2} \right)^{1/2} \mathcal{I}_{e(h)}. \quad (2.65)$$

Here

$$\mathcal{I}_e = \int \psi_{\Gamma_6^+,j,\mathbf{k}_1}^*(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} \psi_{\Gamma_8^-,m,\mathbf{k}_2}(\mathbf{r}) d\mathbf{r}, \quad (2.66)$$

$$\mathcal{I}_h = \int \psi_{\Gamma_7^+,j,\mathbf{k}_1}^*(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} \psi_{\Gamma_8^+,m,\mathbf{k}_2}(\mathbf{r}) d\mathbf{r}. \quad (2.67)$$

In formulas (2.66) and (2.67)  $\psi_{\Gamma m,\mathbf{k}}(\mathbf{r})$  is the Bloch wave function of the electron (hole) in the conduction (valence) band which may be expressed through Wannier



functions localized in the nodes of the lattice:

$$\psi_{\Gamma\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{g}} e^{i\mathbf{kg}} W_{\Gamma}(\mathbf{r} - \mathbf{g}). \quad (2.68)$$

From formulas (2.66) and (2.68) we have

$$\begin{aligned} \mathcal{I}_e &= \delta_{\mathbf{k}_1 - \mathbf{k}_2, \mathbf{q}} \sum_{\mathbf{f}} e^{-i\mathbf{f}(\mathbf{k}_2 + \mathbf{q})} \int W_{\Gamma_6^+ j}^*(\mathbf{r} - \mathbf{f}) e^{i\mathbf{q}\mathbf{r}} W_{\Gamma_8^- m}(\mathbf{r}) d\mathbf{r} \\ &\approx \delta_{\mathbf{k}_1 - \mathbf{k}_2, \mathbf{q}} \int W_{\Gamma_6^+ j}^*(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} W_{\Gamma_8^- m}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (2.69)$$

Since the conduction bands  $\Gamma_6^+$  and  $\Gamma_8^-$  are formed mainly from  $4s$  and  $4p$  states of the copper atom, to estimate the integral (2.69) we can use as functions  $W_{\Gamma_6^+}$  and  $W_{\Gamma_8^-}$  the atomic functions  $\Psi_{4s}$  and  $\Psi_{4p}$ . If by this we preserve in  $\mathcal{I}_e$  (that depends on  $\mathbf{q}$ ) only the term which gives the biggest contribution in summation (integration) over  $\mathbf{q}$  into (2.64), then from (2.65) we obtain the following expression for  $\theta_e(q)$ :

$$\theta_e(q) \cong i \left( \frac{2\pi e^2 \hbar \omega_0}{\varepsilon^* \mathcal{V}_0} \right)^{1/2} \frac{\sqrt{5} a_s}{[1 + (a_s q/2)^2]^3}, \quad (2.70)$$

in which the radius of the copper atom  $4a_B/Z_a$  is replaced by the radius  $a_s$  of the atom in the crystal.

In order to obtain the expression for  $\theta_h(\mathbf{k}, \mathbf{q}; j, m)$  we use the wave functions of the valence electron in the bands  $\Gamma_7^+$  and  $\Gamma_8^+$  [328]:

$$\begin{aligned} \psi_{\Gamma_7^+, 1/2} &= -\frac{i\mathcal{A}}{\sqrt{3}} \frac{R_{32}(r)}{r^2} [XY|\alpha\rangle + (YZ + iXZ)|\beta\rangle], \\ \psi_{\Gamma_7^+, -1/2} &= -\frac{i\mathcal{A}}{\sqrt{3}} \frac{R_{32}(r)}{r^2} [-XY|\beta\rangle + (YZ - iXZ)|\alpha\rangle], \\ \psi_{\Gamma_8^+, 3/2} &= \frac{i\mathcal{A}}{\sqrt{6}} \frac{R_{32}(r)}{r^2} [2XY|\beta\rangle + (YZ - iXZ)|\alpha\rangle], \\ \psi_{\Gamma_8^+, 1/2} &= -\frac{i\mathcal{A}}{\sqrt{2}} \frac{R_{32}(r)}{r^2} (YZ - iXZ)|\beta\rangle, \\ \psi_{\Gamma_8^+, -1/2} &= \frac{i\mathcal{A}}{\sqrt{2}} \frac{R_{32}(r)}{r^2} (YZ + iXZ)|\alpha\rangle, \\ \psi_{\Gamma_8^+, -3/2} &= \frac{i\mathcal{A}}{\sqrt{6}} \frac{R_{32}(r)}{r^2} [2XY|\alpha\rangle - (YZ + iXZ)|\beta\rangle], \end{aligned} \quad (2.71)$$

where  $|\alpha\rangle$  and  $|\beta\rangle$  are the spin functions,  $R_{32}(r)$  is the radial function of the  $3d$  state of the copper ion, and  $\mathcal{A}$  is the normalization constant.



Using (2.65), (2.67), and (2.71), we obtain

$$\theta_h(q) \cong i \left( \frac{2\pi e^2 \hbar \omega_0}{\varepsilon^* \mathcal{V}_0} \right)^{1/2} \frac{q a_i^2}{[1 + (a_i q/2)^2]^5} \cdot \frac{2\sqrt{2}}{3}. \quad (2.72)$$

As in the previous case, we preserved in (2.72) only the term which will give the biggest contribution in integration over  $\mathbf{q}$ . The radius of the copper ion  $3a_B/Z_i$  was replaced by the radius  $a_i$  of the ion in the crystal.

The addition to the electron energy in the conduction band  $\Gamma_6^+$  due to electron-phonon scattering with transition of the electron from band  $\Gamma_6^+(\Gamma_8^-)$  to band  $\Gamma_8^-(\Gamma_6^+)$  according to (2.64) and (2.70) is determined by the expression [325–327]

$$\Delta_{\Gamma_6^+}^{\text{inter}} \approx -\frac{35e^2}{64\varepsilon^* a_s} \cdot \frac{\hbar \omega_0}{E_B - E_Y + \hbar \omega_0 + \hbar^2 q_{1\text{max}}^2/2m_{\Gamma_8^-}}, \quad (2.73)$$

where  $E_B$  and  $E_Y$  are the energy gaps for the blue and yellow series, respectively. The value  $q_{1\text{max}} = \frac{2}{\sqrt{5}} a_s^{-1}$  is found from the condition of the maximum of function

$$f_1(q) = q^2/[1 + (q a_s/2)^2]^6.$$

For the corrections to the energies of holes in bands  $\Gamma_7^+$  and  $\Gamma_8^+$  influenced by interband scattering  $\Gamma_7^+ \rightleftharpoons \Gamma_8^+$  of holes on phonons, on the basis of formulas (2.64) and (2.72) we get [325–327]

$$\begin{aligned} \Delta_{\Gamma_7^{+*}}^{\text{inter}} &\approx \frac{0.031e^2}{\varepsilon^* a_i} \cdot \frac{\hbar \omega_0}{E_G - E_Y + \hbar \omega_0 + \hbar^2 q_{2\text{max}}^2/2m_{\Gamma_8^+}}, \\ \Delta_{\Gamma_8^{+*}}^{\text{inter}} &\approx -\frac{0.031e^2}{\varepsilon^* a_i} \cdot \frac{\hbar \omega_0}{E_G - E_Y - \hbar \omega_0 - \hbar^2 q_{2\text{max}}^2/2m_{\Gamma_7^+}}. \end{aligned} \quad (2.74)$$

Here  $E_G$  is the energy gap for the green series, and  $q_{2\text{max}} = a_i^{-1}$  is determined from the condition of the maximum of the function

$$f_2(q) = q^4/[1 + (q a_i/2)^2]^{10}. \quad (2.75)$$

The numerical estimations of the values of the shifts of bands  $\Gamma_6^+$ ,  $\Gamma_8^-$ ,  $\Gamma_7^+$ , and  $\Gamma_8^+$  and the corresponding shifts of exciton levels at inter- and intraband scattering of electrons and holes on phonons were determined according to formulas (2.63), (2.73), and (2.74) at the following values of the parameters [325–330]:  $E_Y = 17523 \text{ cm}^{-1}$ ,  $E_G = 18588 \text{ cm}^{-1}$ ,  $E_B = 21220 \text{ cm}^{-1}$ ,  $m_{\Gamma_6^+} = 0.99m_0$ ,  $m_{\Gamma_8^-} = 0.26m_0$ ,  $m_{\Gamma_7^+} = 0.69m_0$ ,  $m_{\Gamma_8^+} = 1.776m_0$ ,  $\varepsilon_0 = 7.5$ ,  $\varepsilon_\infty = 6.25$ ,  $\hbar \omega_0 = 660 \text{ cm}^{-1}$ ,  $a_s = 0.8d$ , and  $a_i = 0.4d$  ( $d = 4.263 \text{ \AA}$  is the constant of the lattice). The results are given in Tables 2.1 and 2.2.



**Table 2.1** The energy shift of bands  $\Gamma_6^+$ ,  $\Gamma_7^+$ , and  $\Gamma_8^+$  at intra- and interband scattering of electrons and holes on the longitudinal optical phonons of symmetry  $\Gamma_4^-$  before and after isotopic substitution  $^{16}\text{O} \rightarrow ^{18}\text{O}$  in Cu<sub>2</sub>O crystals

	$\Delta_{\Gamma_6^+}^{\text{intra}}$ (cm <sup>-1</sup> )	$\Delta_{\Gamma_6^+}^{\text{inter}}$ (cm <sup>-1</sup> )	$\Delta_{\Gamma_7^+}^{\text{intra}}$ (cm <sup>-1</sup> )	$\Delta_{\Gamma_7^+}^{\text{inter}}$ (cm <sup>-1</sup> )	$\Delta_{\Gamma_8^+}^{\text{intra}}$ (cm <sup>-1</sup> )	$\Delta_{\Gamma_8^+}^{\text{inter}}$ (cm <sup>-1</sup> )
Before isotopic substitution	-227.28	-26.57	-190.8	4.91	-306.11	2.53
After isotopic substitution	-222.93	-25.62	-187.1	4.735	-300.17	2.43
Isotopic shift	4.35	1	3.7	-0.18	5.94	-0.10

**Table 2.2** The change of energy gaps  $E_Y$  and  $E_G$  for the yellow and green exciton series of the crystal Cu<sub>2</sub>O and energies of the interserial transitions  $Y \rightleftharpoons G$  at intra- and interserial scattering of electrons and holes on the longitudinal optical phonon  $\Gamma_4^-$  before and after isotopic substitution  $^{16}\text{O} \rightarrow ^{18}\text{O}$ 

	$\Delta E_Y$ (cm <sup>-1</sup> )	$\Delta E_G$ (cm <sup>-1</sup> )	$G \rightleftharpoons Y$ (cm <sup>-1</sup> )
Before isotopic substitution	-67.96	49.73	–
After isotopic substitution	-66.185	-49.19	–
Isotopic shift	1.775	-0.54	2.315

From Table 2.2 it is seen that under conditions of independence of the exciton Rydberg constant on the isotopic substitution that was observed experimentally in the crystal Cu<sub>2</sub>O [322, 323], upon substitution of  $^{16}\text{O}$  by  $^{18}\text{O}$ , all resonance lines are shifted by the same value to shorter wavelengths, due to interserial exciton transitions of the yellow and green series. Analogical isotopic shifts are also characteristic for other intraserial exciton transitions in Cu<sub>2</sub>O (yellow  $\rightleftharpoons$  blue, blue  $\rightleftharpoons$  green series).

The fine structure of the exciton absorption spectrum in Cu<sub>2</sub>O crystals is experimentally well studied up to  $n = 10$  [329, 331]. The large number of exciton states manifested in this case allows us to carry out interserial resonances and use them to investigate the isotopic effects. In particular, at electric dipole transitions between the exciton levels  $1SG(^4P_{3/2})$  and  $2PY(^2P_{3/2})$  of the green and yellow series (absorption of long-wavelength IR radiation), the distance between which is  $\hbar\omega_{1SG \rightarrow 2PY} = E_{2PY}(^2P_{3/2}) - E_{1SG}(^4P_{3/2}) = 76.63 \text{ cm}^{-1}$  [329], the relative isotopic shift has the value  $\Delta\omega_{1SG \rightarrow 2PY}/\omega_{1SG \rightarrow 2PY} = 1.72 \cdot 10^{-2}$ . The relative isotopic shift becomes even bigger with a decrease in the frequency of transition. Thus for the interserial paraelectric exciton transitions  $5SG \rightleftharpoons 5PY$  (the distance between the exciton levels in this case is  $1.61 \text{ cm}^{-1}$ ) the relative isotopic shift is equal to  $\Delta\omega_{5SG \rightarrow 5PY}/\omega_{5SG \rightarrow 5PY} = 0.82$ . For this transition, as is seen, the shifts of the resonance frequency at isotopic substitution are on an order comparable with the frequency of the transition, e.g., the isotopic shift in this case is giant.

Calculation of the interaction of electrons and holes with optical phonons by means of the deformation potential may slightly change the values of the isotopic



shift. For intraband scattering processes the ratio of the square modules of the electron (hole)–phonon coupling constants by deformation and polarization interactions is determined by the expression [332]

$$\frac{|\vartheta_{e(h)}^{\text{def}}(\mathbf{q})|^2}{|\vartheta_{e(h)}^{\text{pol}}(\mathbf{q})|^2} = \frac{T_{\mathbf{q}}}{\hbar\omega_0}, \quad T_{\mathbf{q}} = \frac{\hbar^2 \mathbf{q}^2}{2m_{e(h)}}. \quad (2.76)$$

Thus, at low values of the quasi-impulses and large phonon energies, the polarization interaction is determining. According to (2.76) in  $\text{Cu}_2\text{O}$  crystals the interaction of the electrons in band  $\Gamma_6^+$  and the holes in bands  $\Gamma_7^+$  and  $\Gamma_8^+$  with the longitudinal optical phonon of symmetry  $\Gamma_4^-$  by deformation potential becomes actual only with values of the wave vectors of the phonons equal, respectively, to  $1.46 \cdot 10^7 \text{ cm}^{-1}$ ,  $1.22 \cdot 10^7 \text{ cm}^{-1}$ , and  $1.95 \cdot 10^7 \text{ cm}^{-1}$ .

In concluding this section, we remark that on the basis of measurements of the isotopic shifts of interserial exciton resonances, from (2.64)–(2.75), the radii  $a_s$  and  $a_i$  of the atom and the copper ion, respectively, in  $\text{Cu}_2\text{O}$  crystals can be determined.



<http://www.springer.com/978-3-642-35806-7>

Resonance Effects of Excitons and Electrons

Basics and Applications

Geru, I.; Suter, D.

2013, XVII, 283 p. 36 illus., 14 illus. in color., Softcover

ISBN: 978-3-642-35806-7