Application of the method of projective representations to the analysis of exciton-phonon transitions in enantiomorphous tetragonal crystals ZnP₂ and CdP₂

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Abstract. The projective representations of the wavevector group were applied to the analysis of exciton-phonon transitions in enantiomorphous tetragonal crystals ZnP₂ and CdP₂. Selection rules for indirect transitions were derived. Using $\vec{k}\vec{p}$-method, the different points in the Brillouin zone were examined to identify zero slopes and extremums of the dispersion curves $E(\vec{k})$. Photoluminescence and edge absorption polarized spectra were interpreted taking into account the results of above theoretical analysis.

Keywords: projective representations, exciton-phonon transitions, α-ZnP₂, CdP₂.

Symmetry analysis helps to predict some basic features of electronic transitions that appear as bands in optical spectra. The transition probability is defined by the product of the squared transition matrix element and combined density of states. Symmetry analysis gives selection rules, i.e., it shows what matrix elements are non-zero. The high density of states is expected in the vicinity of points with zero slope and/or extremums of the energy dispersion curves $E(\vec{k})$.

In this paper, we represent the method of selection rule calculations for exciton-phonon transitions in the tetragonal enantiomorphous crystals α-ZnP₂ and CdP₂. These crystals belong to $P4_12_12$ or $P4_32_12$ space symmetry groups. Earlier projective representations were used for analysis of one- and two-phonon Raman spectra of the same crystals [1, 2].

The tetragonal crystals of zinc and cadmium diphosphides are indirect semiconductors, so it is necessary to examine interband transitions between different points of the Brillouin zone (Fig. 1). Here we examine the high symmetry points Γ ($\vec{k}_\Gamma = 0$), Z ($\vec{k}_Z = -\dfrac{\vec{b}_1}{2}$), A ($\vec{k}_A = -\dfrac{\vec{b}_1}{2} - \dfrac{\vec{b}_2}{2} - \dfrac{\vec{b}_3}{2}$), M ($\vec{k}_M = -\dfrac{\vec{b}_2}{2} - \dfrac{\vec{b}_3}{2}$), X ($\vec{k}_X = -\dfrac{\vec{b}_2}{2}$) and X' ($\vec{k}_{X'} = -\dfrac{\vec{b}_3}{2}$), R ($\vec{k}_R = -\dfrac{\vec{b}_1}{2} - \dfrac{\vec{b}_2}{2}$) and R' ($\vec{k}_{R'} = -\dfrac{\vec{b}_1}{2} - \dfrac{\vec{b}_3}{2}$). Points Γ, Z, A, and M possess full symmetry of the point group 422 as well as X, X', R, and R' ones belong to the point group 222. To calculate selection rules and to ascertain whether the mentioned points are those of band extremums, it is necessary to know irreducible representations of wavevector groups. The irreducible representations of the wavevector groups can be found using the method of projective representations [1, 3].

To derive the selection rules for exciton-phonon transitions, we need to know representations both for phonon and electron states. The electron states are transformed according to the representations Γ_6, Γ_7, $(Z_1 + Z_2)$, $(Z_3 + Z_4)$, Z_5, $(A_1 + A_3)$, $(A_2 + A_4)$, $((A_5))\cdot(M_6 + M_7)$, $(X_1 + X_3)$, $(X_2 + X_4)$, $(X'_1 + X'_4)$, $(X'_2 + X'_3)$, $((R_5))$, and $((R'_5))$. The phonon states are transformed according to the representations $\Gamma_1 - \Gamma_5$, Z_6, Z_7, $(A_6 + A_7)$, $(M_1 + M_4)$, $(M_2 + M_3)$, M_5, X_5, $(R_1 + R_4)$, $(R_2 + R_3)$, $(R'_1 + R'_3)$, and $(R'_2 + R'_4)$. Parentheses are for merging of complex conjugated representations. Double parentheses are for duplication of two-dimensional representations. The merging and duplication of representations are caused by the invariance with respect to the time inversion and governed by the Herring criterion [4]. The projective representations for Λ, S, V, Σ, Δ, W, and U points depend on the wavevector [3]. Their evolution in certain direction can be pictured graphically as shown in Fig. 2 for $\Gamma - \Sigma - M$.
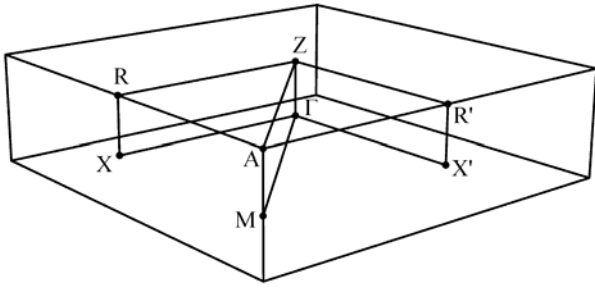
Fig. 1. Schematic drawing of the Brillouin zone that corresponds to tetragonal crystals of space symmetry groups $P4_12_12$ and $P4_32_12$.
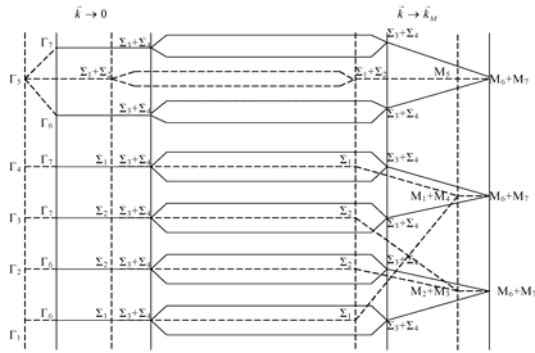

Fig. 2. Evolution of representations in $\Gamma - M$ direction for groups $P4_12_12$ (solid line – electron states, dashed line – phonon states).

Fig. 3. Photoluminescence spectra of tetragonal crystals ZnP_2 (a) and CdP_2 (b).

The selection rules for exciton-phonon transitions follow from the formula:

$$N_0^{\text{ex}-\text{ph}} = \frac{1}{h} \sum_{g \in G_{\bar{k}}} \chi_{\bar{k}'\mu}^*(g)\chi_s(g)\chi_\kappa(g)\chi_{\bar{k}\nu}(g)\chi_{\bar{q}\eta}(g),$$

where $\chi_{\bar{k}'\mu}^*(g)$ and $\chi_{\bar{k}\nu}(g)$ are characters of representations of hole and electron states in valence and conduction bands, respectively; $\chi_s(g)$ is the character of representation of the dipole transition operator; $\chi_\kappa(g)$ is the character of the hole and electron moving relatively to their center of gravity, $\chi_{\bar{q}\eta}(g)$ is the character of the phonon state representation. For the allowed transition $N_0^{\text{ex}-\text{ph}} \neq 0$, and for the forbidden one $N_0^{\text{ex}-\text{ph}} = 0$. If any external magnetic field is absent, the characters of merged representations have to be used (selection rules are shown in Table 1).

For the point $\bar{k}_0$ with zero slope of energy dispersion curves, the condition $dE(\bar{k}_0)\big/dk_\alpha = 0$ should be fulfilled. In addition, in the point of extremum the components of inverse effective mass tensor $1\big/m_{\alpha\beta}$
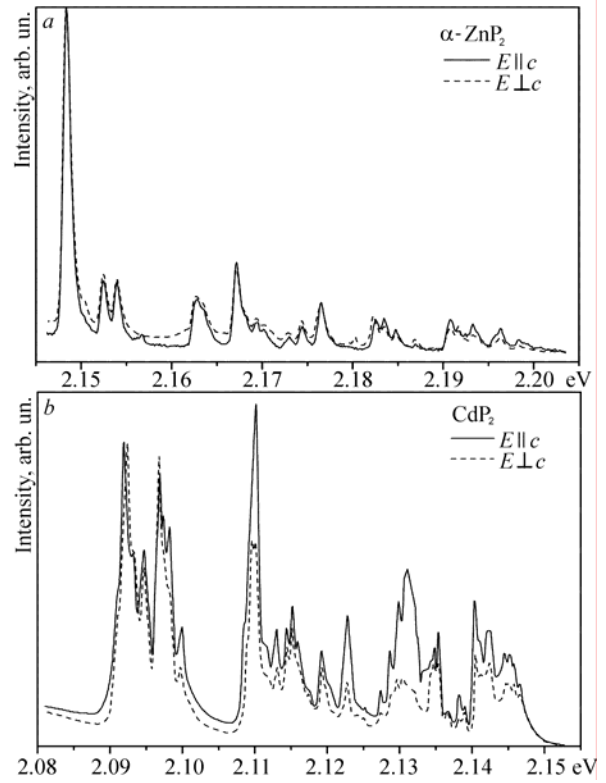
should not be equal to zero. We have analyzed using the $\bar{kp}$-method [4] whether examined points are the critical ones (results are summarized in Tables 2 and 3). From Table 3, it is easy to see that there are non-zero components of the inverse effective mass tensor $\frac{1}{m_{\alpha\beta}}$ in every examined point of the Brillouin zone. It means that some dispersion curves of $E(\bar{k})$ may have the extremum in these points. But not all points are those of zero slope (see Table 2). There is no point in the Brillouin zone that has all zero components $dE(\bar{k}_0)\big/dk_\alpha$ for both electron and phonon states.

Photoluminescence and absorption polarized spectra of α-ZnP_2 and CdP_2 (Figs 3, 4) were obtained at the temperature 1.7 K using a spectrometer DFS-24 with the resolution less than 1 cm^{-1} at $\lambda = 550$ nm. Photoluminescence was excited by radiation of Ar$^+$ laser ($\lambda = 514.5$ nm) with the output power 900 mW. The main feature of photoluminescence spectra in both polarizations (Fig. 3) is the equal number of bands with approximately the same phonon energies. It means that all the observed interband transitions are allowed in both polarizations.

Table 1. Selection rules for exciton-phonon transitions between different points of the Brillouin zone in tetragonal crystals ZnP_2 and CdP_2.

| Type of transition	Allowed transitions	Forbidden transitions
$\Gamma - Z$	$\Gamma_2 \subset \Gamma_6 \times (Z_1+Z_2) \times Z_7, \Gamma_6 \times (Z_3+Z_4) \times Z_6, \Gamma_6 \times Z_5 \times Z_6, \Gamma_6 \times Z_5 \times Z_7,$ $\Gamma_7 \times (Z_1+Z_2) \times Z_6, \Gamma_7 \times (Z_3+Z_4) \times Z_7, \Gamma_7 \times Z_5 \times Z_6, \Gamma_7 \times Z_5 \times Z_7$ $\Gamma_5 \subset \Gamma_6 \times (Z_1+Z_2) \times Z_6, \Gamma_6 \times (Z_1+Z_2) \times Z_7, \Gamma_6 \times (Z_3+Z_4) \times Z_6,$ $\Gamma_6 \times (Z_3+Z_4) \times Z_7, \Gamma_6 \times Z_5 \times Z_6, \Gamma_6 \times Z_5 \times Z_7, \Gamma_7 \times (Z_1+Z_2) \times Z_6,$ $\Gamma_7 \times (Z_1+Z_2) \times Z_7, \Gamma_7 \times (Z_3+Z_4) \times Z_6, \Gamma_7 \times Z_5 \times Z_6, \Gamma_7 \times Z_5 \times Z_7$	$\Gamma_2 \subset \Gamma_6 \times (Z_1+Z_2) \times Z_6, \Gamma_6 \times (Z_3+Z_4) \times Z_7,$ $\Gamma_7 \times (Z_1+Z_2) \times Z_7, \Gamma7 \times (Z_3+Z_4) \times Z_6$ $\Gamma_5 \subset 0$
$\Gamma - A$	$\Gamma_2 \subset \Gamma_6 \times (A_1+A_2) \times (A_6+A_7), \Gamma_6 \times (A_3+A_4) \times (A_6+A_7),$ $\Gamma_6 \times 2A_5 \times (A_6+A_7), \Gamma_7 \times (A_1+A_2) \times (A_6+A_7),$ $\Gamma_7 \times (A_3+A_4) \times (A_6+A_7), \Gamma_7 \times 2A_5 \times (A_6+A_7)$ $\Gamma_5 \subset \Gamma_6 \times (A_1+A_2) \times (A_6+A_7), \Gamma_6 \times (A_3+A_4) \times (A_6+A_7),$ $\Gamma_6 \times 2A_5 \times (A_6+A_7), \Gamma_7 \times (A_1+A_2) \times (A_6+A_7),$ $\Gamma_7 \times (A_3+A_4) \times (A_6+A_7), \Gamma_7 \times 2A_5 \times (A_6+A_7)$	$\Gamma_2 \subset 0$ $\Gamma_5 \subset 0$
$\Gamma - M$	$\Gamma_2 \subset \Gamma_6 \times (M_1+M_2) \times (M_6+M_7), \Gamma_6 \times (M_3+M_4) \times (M_6+M_7),$ $\Gamma_6 \times M_5 \times (M_6+M_7), \Gamma_7 \times (M_1+M_2) \times (M_6+M_7),$ $\Gamma_7 \times (M_3+A_4) \times (M_6+M_7), \Gamma_7 \times 2M_5 \times (M_6+M_7)$ $\Gamma_5 \subset \Gamma_6 \times (M_1+M_2) \times (M_6+M_7), \Gamma_6 \times (M_3+M_4) \times (M_6+M_7),$ $\Gamma_6 \times M_5 \times (M_6+M_7), \Gamma_7 \times (M_1+M_2) \times (M_6+M_7),$ $\Gamma_7 \times (M_3+A_4) \times (M_6+M_7), \Gamma_7 \times 2M_5 \times (M_6+M_7)$	$\Gamma_2 \subset 0$ $\Gamma_5 \subset 0$
$\Gamma - X$	$\Gamma_2 \subset \Gamma_6 \times (X_1+X_3) \times X_5,$ $\Gamma_6 \times (X_2+X_4) \times X_5,$ $\Gamma_7 \times (X_1+X_3) \times X_5,$ $\Gamma_7 \times (X_2+X_4) \times X_5$ $\Gamma_5 \subset \Gamma_6 \times (X_1+X_3) \times X_5,$ $\Gamma_6 \times (X_2+X_4) \times X_5,$ $\Gamma_7 \times (X_1+X_3) \times X_5,$ $\Gamma_7 \times (X_2+X_4) \times X_5$	$\Gamma_2 \subset 0$ $\Gamma_5 \subset 0$
$\Gamma - X'$	$\Gamma_2 \subset \Gamma_6 \times (X'_1+X'_4) \times X'_5,$ $\Gamma_6 \times (X'_2+X'_3) \times X'_5,$ $\Gamma_7 \times (X'_1+X'_4) \times X'_5,$ $\Gamma_7 \times (X'_2+X'_3) \times X'_5$ $\Gamma_5 \subset \Gamma_6 \times (X'_1+X'_4) \times X'_5,$ $\Gamma_6 \times (X'_2+X'_3) \times X'_5,$ $\Gamma_7 \times (X'_1+X'_4) \times X'_5,$ $\Gamma_7 \times (X'_2+X'_3) \times X'_5$	$\Gamma_2 \subset 0$ $\Gamma_5 \subset 0$

Γ – R	$\Gamma_2 \subset \Gamma_6 \times ((R_5)) \times (R_1+R_4),$	$\Gamma_2 \subset 0$
	$\Gamma_6 \times ((R_5)) \times (R_2+R_3),$	
	$\Gamma_7 \times ((R_5)) \times (R_1+R_4),$	
	$\Gamma_7 \times ((R_5)) \times (R_2+R_3)$	
	$\Gamma_5 \subset \Gamma_6 \times ((R_5)) \times (R_1+R_4),$	$\Gamma_5 \subset 0$
	$\Gamma_6 \times ((R_5)) \times (R_2+R_3),$	
	$\Gamma_7 \times ((R_5)) \times (R_1+R_4),$	
	$\Gamma_7 \times ((R_5)) \times (R_2+R_3)$	
Γ – R'	$\Gamma_2 \subset \Gamma_6 \times ((R'_5)) \times (R'_1+R'_3),$	$\Gamma_2 \subset 0$
	$\Gamma_6 \times ((R'_5)) \times (R'_2+R'_4),$	
	$\Gamma_7 \times ((R'_5)) \times (R_1+R'_3),$	
	$\Gamma_7 \times ((R'_5)) \times (R'_2+R'_4)$	
	$\Gamma_5 \subset \Gamma_6 \times ((R'_5)) \times (R'_1+R'_3),$	$\Gamma_5 \subset 0$
	$\Gamma_6 \times ((R'_5)) \times (R'_2+R'_4),$	
	$\Gamma_7 \times ((R'_5)) \times (R'_1+R'_3),$	
	$\Gamma_7 \times ((R'_5)) \times (R'_2+R'_4)$	

Table 2. Number of components of momentum for different points in the Brillouin zone of crystals ZnP_2 and CdP_2.

Representation	Number of components $dE(\vec{k}_0)/dk_\alpha \neq 0$		
	$\parallel z$	$\perp z$	
$\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$	0	0	
Γ_5	1	0	
Γ_6, Γ_7	1	1	
$(Z_1+Z_2), (Z_3+Z_4)$	2 diagonal; 2 non-diagonal	0 diagonal; 0 non-diagonal	
Z_5	1	0	
Z_6, Z_7	0	0	
$(M_1+M_4), (M_2+M_3)$	0 diagonal; 0 non-diagonal	0 diagonal; 0 non-diagonal	
M_5	1	0	
(M_6+M_7)	2 diagonal; 1 non-diagonal	2 diagonal; 3 non-diagonal	
	in Γ - A direction		
$(A_1+A_3), (A_2+A_4)$	0 diagonal; 0 non-diagonal		
$((A_5))$	4 diagonal; 3 non-diagonal		
(A_6+A_7)	6 diagonal; 2 non-diagonal		
	$\parallel z$	$\parallel x$	$\parallel y$
$(X_1+X_3), (X_2+X_4)$	0 diagonal; 0 non-diagonal	2 diagonal; 2 non-diagonal	0 diagonal; 0 non-diagonal
X_5	0	1	0
$(X'_1+X'_4), (X'_2+X'_3)$	0 diagonal; 0 non-diagonal	0 diagonal; 0 non-diagonal	2 diagonal; 2 non-diagonal
X'_5	0	0	1
$(R_1+R_4), (R_2+R_3)$	0 diagonal; 0 non-diagonal	0 diagonal; 0 non-diagonal	2 diagonal; 2 non-diagonal
$((R_5))$	4 diagonal; 1 non-diagonal	4 diagonal; 1 non-diagonal	4 diagonal; 2 non-diagonal
$(R'_1+R'_3), (R'_2+R'_4)$	0 diagonal; 0 non-diagonal	2 diagonal; 2 non-diagonal	0 diagonal; 0 non-diagonal
$((R'_5))$	4 diagonal; 1 non-diagonal	4 diagonal; 2 non-diagonal	4 diagonal; 1 non-diagonal

Table 3. Number of components of inverse effective mass tensor for different points in the Brillouin zone of crystals ZnP_2 and CdP_2.

Representation	Number of components $\dfrac{1}{m_{\alpha\beta}}$	
	$\parallel z$	$\perp z$
$\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$	1	1
Γ_5	1	3
Γ_6, Γ_7	1	1
$(M_1+M_4), (M_2+M_3)$	2 diagonal; 1 non-diagonal	4 diagonal; 3 non-diagonal
M_5	1	2
(M_6+M_7)	2 diagonal; 1 non-diagonal	6 diagonal; 3 non-diagonal
$(A_1+A_3), (A_2+A_4)$	6 diagonal; 2 non-diagonal	
$((A_5))$	16 diagonal; 6 non-diagonal	
(A_6+A_7)	12diagonal; 6 non-diagonal	
$(Z_1+Z_2), (Z_3+Z_4)$	2 diagonal; 2 non-diagonal	
Z_5	2	
Z_6, Z_7	3	
$(X_1+X_3), (X_2+X_4)$	8 diagonal; 3 non-diagonal	
X_5	2	
$(X'_1+X'_4), (X'_2+X'_3)$	8 diagonal; 3 non-diagonal	
X'_5	2	
$(R_1+R_4), (R_2+R_3)$	8 diagonal; 3 non-diagonal	
$((R_5))$	24 diagonal; 16 non-diagonal	
$(R'_1+R'_3), (R'_2+R'_4)$	8 diagonal; 3 non-diagonal	
$((R'_5))$	24 diagonal; 16 non-diagonal	
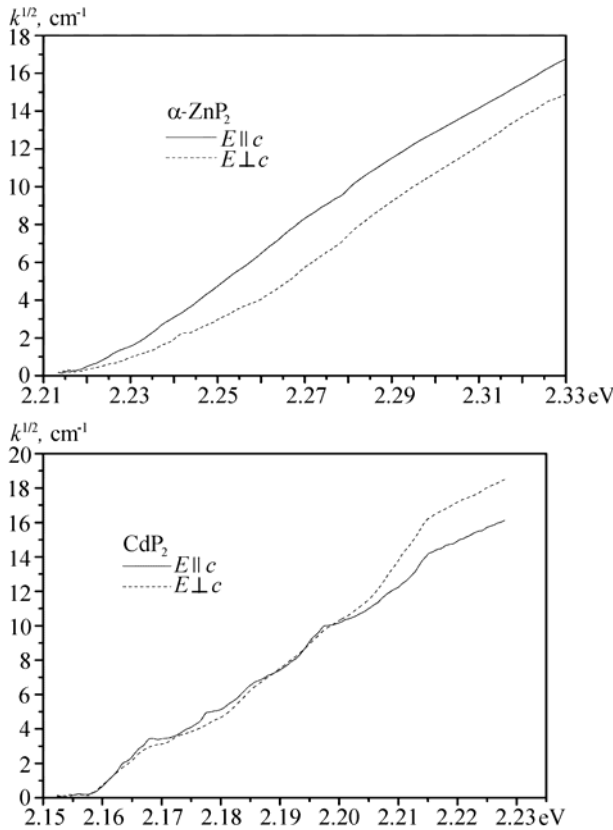
Fig. 4. Edge absorption spectra of tetragonal crystals ZnP_2 and CdP_2.

Comparing the spectra of exciton-phonon transitions, phonon Raman scattering [1, 2], and taking into consideration the results of our symmetry analysis (see Tables 1, 2, and 3) we can suppose that the minimum of conduction band may be located in M point. There are two considerations for this conclusion: 1) all $\Gamma - M$ transitions are allowed in both polarizations, but some of $\Gamma - Z$ transitions are forbidden in $\vec{E}\parallel z$ polarization (it was mentioned that the main feature of the obtained photoluminescence spectra (Fig. 2) is the equal number of bands with approximately the same phonon energies in both polarizations); 2) for electrons in M point, there are minimal number of non-zero components $dE(\vec{k}_0)/dk_\alpha$ in $\Gamma - M$ direction and M point is the point of zero slope for all the dispersion curves of phonon states in the same direction. The points Z and R are not those of zero slope for all dispersion curves of electron states in the corresponding directions. In the point A, there are non-zero components $dE(\vec{k}_0)/dk_\alpha$ both for electron and phonon states. Additional criteria to further selection of a candidate for the conduction band extremum can be obtained from the measurements of free-exciton luminescence in magnetic fields when the degeneration of energy states will be removed as caused by merging the states. For instance, the energy dispersion curves in $\Gamma - M$ direction that corresponds to non-merged states M_6 and M_7 will have zero slope in M point.

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